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HEXAMETHYLENE DIISOCYANATE FUNCTIONALIZED GRAPHENE OXIDE AS A FILLER IN POLYURETHANE AND POLYANILINE COMPOSITES

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 24 June, 2014.

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Abstract of master's thesis

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Abstract

Graphene is a carbon nanomaterial with high electrical and thermal conductivities, high mechanical strength, good barrier properties, and interesting optical properties. The purpose of this thesis is to study the possible functionalizations of graphene and the use of such functionalized materials in composites.

In its pure form, graphene is insoluble in most solvents and it has no functional groups that could be easily covalently functionalized, complicating its use in composite materials. To introduce such functional groups, graphene can be oxidized to form waterdispersible graphene oxide. In addition to introducing oxygen functionalities to the material, the oxidation process also disrupts graphene's structure and conductivity. Most of the conductivity can be restored by reduction, and after reduction the material still has a small amount of oxygen functionalities left that can be used for covalent functionalization.

The main purpose for functionalizing graphene is to increase its solubility. Other purposes include grafting polymers to graphene's surface, doping, and bandgap creation.

In the experimental part of this work we study the functionalization of graphene oxide with a chemical that has two functional groups. For this purpose, hexamethylene diisocyanate was chosen, as isocyanate can form urethanes with the hydroxyl groups of graphene oxide. The functionalized material was then studied as the filler in polyaniline and polyurethane composites. The composition of the fabricated materials was studied with infrared spectroscopy, thermal properties were studied with differential scanning calorimetry and transient plane source method, and the electrical conductivites were studied with 4-point probe method.

The IR spectra show succesful functionalization of graphene oxide, and the succesful integration of functionalized graphene oxide to the matrix polymer. The electrical conductivity of polyaniline composites increased somewhat, but the polyurethane composites were not electrically conducting. No significant changes were observed in the thermal conductivites.

Keywords Graphene, Graphene Oxide, Functionalization, Isocyanate, Polyaniline, Polyurethane

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Työn nimi Heksametyleeni-di-isosyanaatti funktionalisoitu grafeenioksidi täyteaineena polyuretaani ja polyaniliini komposiiteissa

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Tiivistelmä

Grafeeni on hiilinanomateriaali, jolla on korkea sähkön- ja lämmönjohtavuus, hyvä mekaaninen kestävyys sekä hyvät kaasunläpäisevyys ja optiset ominaisuudet. Tässä työssä tutkitaan grafeenin funktionalisointimahdollisuuksia sekä funktionalisoidun grafeenin käyttöä komposiiteissa.

Puhtaassa muodossaan grafeeni ei liukene yleisiin liuottimiin, eikä sillä ole funktionaalisia ryhmiä, joita voitaisiin käyttää hyväksi kovalenttisessa funktionalisoinnissa. Tämä hankaloittaa sen käyttöä komposiittimateriaaleissa. Funktionaalisten ryhmien luomiseksi, grafeeni voidaan hapettaa grafeenioksidiksi. Happi-funktionaalisuuksien tuomisen lisäksi, hapettaminen myös vahingoittaa grafeenin rakennetta ja johtavuusominaisuuksia. Johtavuus voidaan kuitenkin suurimmaksi osaksi palauttaa pelkistämällä. Pelkistyksen jälkeen grafeenioksidissa on yhä jäljellä joitakin funktionaalisia ryhmiä, joita voidaan käyttää kovalenttiseen funktionalisointiin.

Grafeenin funktionalisoinnin yleisin tavoite on saada grafeeni liukenemaan, tai ainakin dispergoitumaan, tiettyyn liuottimeen. Muita tavoitteita funktionalisoinnille ovat mm. polymeerien kiinnitys grafeenin pintaan, douppaus, sekä bandgapin luominen.

Työn kokeellisessa osuudessa tutkitaan grafeenin funktionalisointia kemikaalilla, jossa on kaksi funktionaalista ryhmää. Tätä tarkoitusta varten valittiin Heksametyleeni-di-isosyanaatti, sillä isosyanaatti voi muodostaa uretaaneja grafeenioksidin hydroksyyliryhmien kanssa. Tällä tavoin funktionalisoitua materiaalia tuktittiin täyteaineena polyaniliini ja polyuretaani komposiiteissa. Valmistettujen materiaalien rakennetta tutkittiin infrapunaspektroskopialla. Lisäksi komposiiteista mitattiin lämmön- ja sähkönjohtavuudet.

Mitatuista infrapunaspektreistä on nähtävissä, että sekä grafeenioksidin funktionalisointi, että funktionalisoidun materiaalin integrointi polymeeriin onnistuivat. Polyaniliinikomposiitin sähkönjohtavuus kasvoi, mutta polyuretaanikomposiitit eivät johtaneet sähköä. Komposiittien lämmönjohtavuuksissa ei tapahtunut merkittäviä muutoksia.

Avainsanat Grafeeni, Grafeenioksidi, Funktionalisointi, Isosyanaatti, Polyaniliini, Polyuretaani

PREFACE

This work was done in the polymer technology group in Aalto University School of Chemical Technology, Espoo, Finland. The work was supervised by Academy Professor Jukka Seppälä, and instructed by Ph.D. Nguyen Dang Luong both from Aalto University School of Chemical Technology. I thank them for all the valuable advice I have received from them.

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I would also like to thank my family and friends for all the patience and support they have given me while I was struggling with this work, or with myself.

Finally, I dedicate this book to B.Sc. Jari Isaksson in exchange for champagne.

Espoo, 24 June 2014.

Antti Metsälä

Contents

ABBREVIATIONS

AFM	Atomic force microscopy
APTS	3-aminopropyltriethoxysilane
ATRP	Atom transfer radical polymerization
BPO	Benzoyl peroxide
BR	Bulk resistivity
CNT	Carbon nanotube
CS	Chitosan
CSR	Corrected sheet resistance
CVD	Chemical vapor deposition
DCC	*N,N'*-dicyclohexylcarbodiimide
DCM	Dichloromethane
DMF	Dimethylformamid
DSC	Differential scanning calorimetry
EDC	1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide
ER	Electrorheological
FLG	Few-layer graphene
FTIR	Fourier transform infrared spectroscopy
GIC	Graphite intercalation compounds
GO	Graphene oxide
HDI	Hexamethylene diisocyanate
HRP	Horseradish peroxidase
IL	Ionic liquid
ITO	Indium tin oxide
MDI	Methylene diphenyl diisocyanate
NMP	*N*-methyl-2-pyrrolidone
ODA	Octadecylamine
OLED	Organic light-emitting diodes
P3HT	Poly(3-hexylthiophene)
PAAm	Poly(allylamine)
PANI	Polyaniline
PBA	Poly(butyl acrylate)
PBASE	Pyrene butanoic acid succidymidyl ester
PDMAEMA	Poly(2-(dimethylamino)ethyl methacrylate)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEG	Polyethylene glycol

PEO	Poly(ethylene oxide)
PEO-*b*-PPO-*b*-PEO	Poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide)
PFA	Polyfurfuryl alcohol
PMMA	Poly(methyl methacrylate)
PPG	Polypropylene glycol
PPy	Polypyrrole
PS	Polystyrene
PSS	Poly(styrenesulfonate)
PtBA	Poly(tert-butyl acrylate)
PVA	Poly(vinyl alcohol)
RGO	Reduced graphene oxide
SDBS	Sodium dodecylbenzene sulfonate
SR	Sheet resistance
SG	Sulphonated graphene
SLG	Single-layer graphene
SPANI	Sulfonated polyaniline
TC	Thermal conductivity
TCNQ	7,7,8,8-tetracyanoquinodimethane
TD	Thermal diffusivity

LITERATURE SURVEY

1 Introduction

Composites are materials made from two or more different materials. The goal of a composite material is to enhance the properties of an existing material or to tailor a new material for a specific purpose. The applications of composites vary from building materials, such as concrete, to everyday objects, such as hockey sticks, and on to special applications, such as electrodes for supercapacitors.

Currently, composite research concentrates mainly on nanocomposites, which consist of nanosized filler particles and a matrix that is usually a polymer, silicon, or metal. The interest in these composites comes from the discovery of nanomaterials that have excellent properties, e.g. high thermal and electrical conductances, high mechanical strength, and good optical and barrier properties. These nanomaterials include carbon nanomaterials such as nanotubes, fullerene and graphene. The goals of nanocomposites include the enhancing of a materials properties with minimal amount of filler, finding cheap and easy to produce materials for electronic applications, and creating safe and efficient materials for drugs and other medical applications.

Graphene is a carbon nanomaterial with excellent electrical, thermal, mechanical, barrier, and optical properties, which makes it an interesting material for use as a filler in nanocomposites. It can be incorporated to a matrix material by using secondary forces such as π-π interactions and Van der Waals forces, or covalently by using the functionalities of its oxide or reduced oxide. These same methods also offer a wealth of possibilities for functionalizing graphene. As graphene has a wide variety of interesting properties, the applications for its composites also vary greatly ranging from electrode materials to sensors, and from transistors to carrier materials for drugs.

2 Graphene

2.1 Structure

Graphene is a planar allotrope of carbon consisting of sp^2 hybridized carbon atoms in a honeycomb lattice. It is the basic structural element of other carbon allotropes such as carbon nanotubes (CNT), fullerenes and graphite. CNT can be thought of as a rolled graphene sheet, fullerene as a graphene sheet wrapped up, and graphite as a stack of graphene sheets. Figure 1 shows the relation between the aforementioned allotropes. [1]

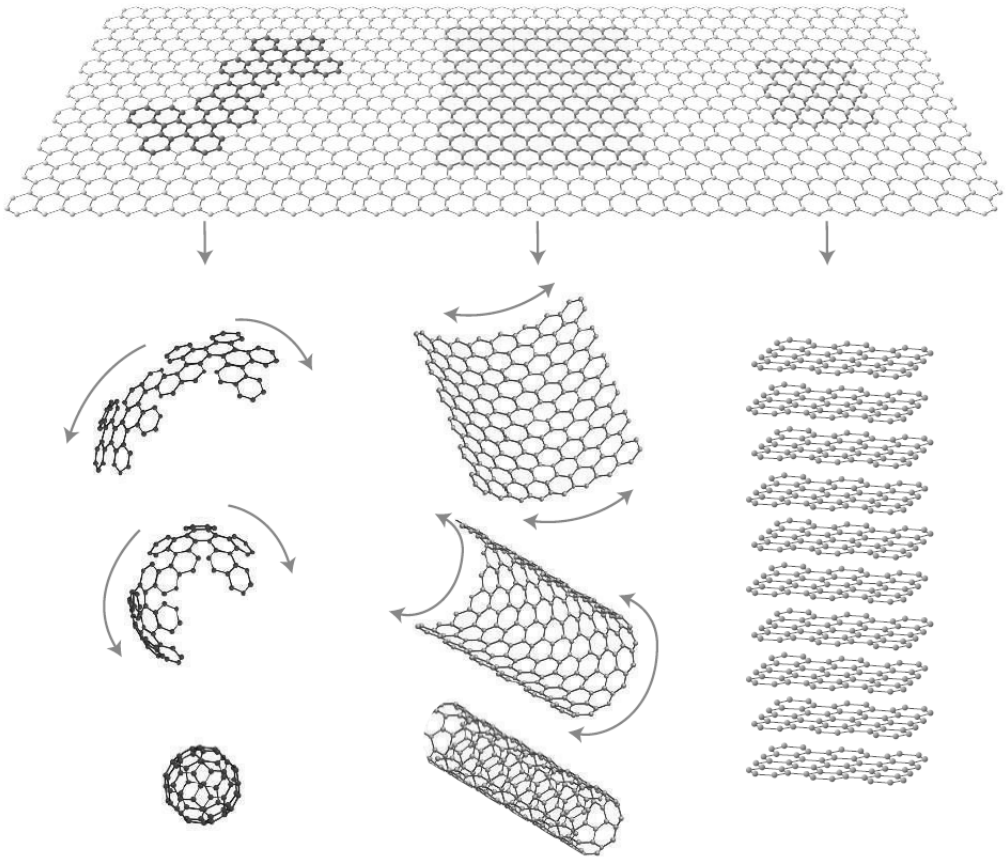


Figure 1. The relation between graphene, fullerene, carbon nantube (CNT) and graphite. [1]

2.2 Properties

For single-layer graphene (SLG), electron mobility of 200 000 $cm^2/(V{\cdot}s)$ has been reached by minimizing impurity scattering [2,3]. For few-layer graphene (FLG), electron mobility of 15 000 $cm^2/(V{\cdot}s)$ has been reported [4].

The Young's modulus and fracture strength of graphene have been studied by atomic force microscopy (AFM). The Young's modulus for defect free graphene was 1.0 TPa and the fracture strength 130 GPa. [5]

The thermal conductivity of grahene depends on the method it is produced by and, to a lesser extent, the substrate graphene is on. A thermal conductivity of 600 $W/(m{\cdot}K)$ was obtained in an experiment that had micromechanically exfoliated graphene deposited onto a SiO_2 substrate [6]. For graphene produced by chemical vapor deposition (CVD) and deposited onto a silicon nitride membrane thermal conductivity was 2500 $W/(m{\cdot}K)$ [7]. A value of 5000 $W/(m{\cdot}K)$ was reached for suspended mechanically exfoliated graphene sheet [8].

The opacity of a graphene sheet has been reported to be 2.3%. For n-layer graphene, the opacity is n times the 2.3%. [9] This means that, in theory, 44 layers of graphene could absorb all incident white light. The light absorbing ability of graphene has been used to create an ultrafast (40 GHz) photodetector [10].

Due to its structure as a 2 dimensional material, carbon is impermeable to any gaseous molecules. This gives graphene and, to a lesser extent, its derivatives excellent barrier properties. [11]

3 Production of Graphene

The production of graphene through mechanical exfoliaiton (the scotch tape method) [4] or epitaxial growth [12,13] is work intensitive and thus not suitable for large scale production. Chemical conversion of graphite into graphene oxide (GO) and its reduction to reduced graphene oxide (RGO) is considered a much

more feasible method for large scale graphene production. [14]

As the structure of RGO contains defects caused by the chemical reactions [15], its properties do not quite match those of pure graphene. On the other hand RGO is more reactive than graphene, because of said defects. In addition, RGO and graphene oxide can be functionalized in many ways for a variety of applications. Figure 2 illustrates the path from graphite to reduced graphene oxide.

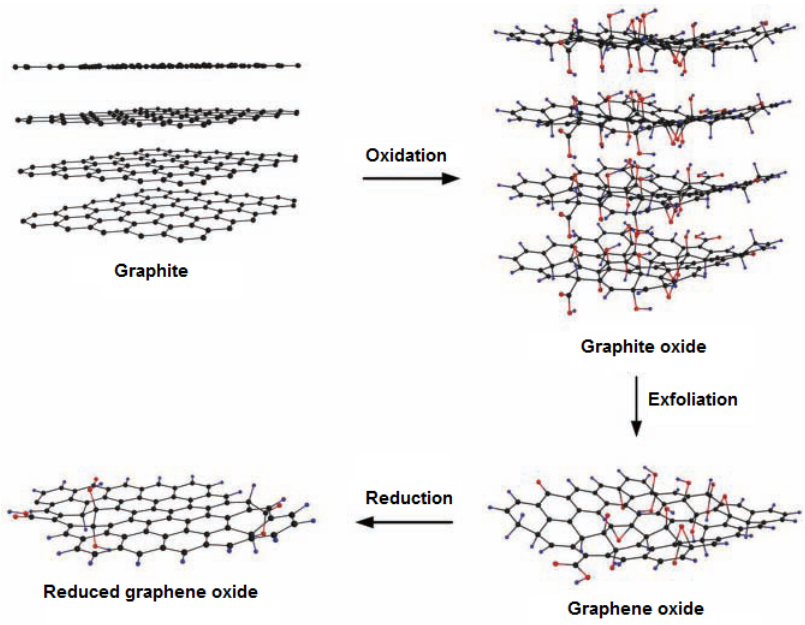


Figure 2. The path from graphite to reduced graphene oxide. [16]

3.1 Graphene Oxide

3.1.1 Structure

The oxidation of graphite and the exfoliation of the formed graphite oxide is a simple method to acquire an aqueous solution of functionalized graphene. Oxidation introduces functional groups such as epoxides, hydroxyls, and carboxyls to graphene. These groups can then be used to covalently attach other functionalities to graphene. Since the oxidation, especially the introduction of epoxides, breaks the sp^2 structure of graphene, graphene oxide (GO) is not electrically conductive. The reduction of GO to create reduced graphene oxide

(RGO) partially returns the sp^2 structure but it also leaves some of the oxygen functionalities. The oxidation and reduction also create defects in the structure of graphene such as holes and rings with 5 or 7 carbon atoms instead of the 6 in pure graphene [15]. It is important to note that GO is a non-stoichiometric material. Its structure and properties depend on the method it is synthesized by and the amount of oxygen functionalities introduced. [16–18]

The exact chemical structure of graphene oxide depends on the graphite used, and the method and level of oxidation. It is generally thought that the oxygen is bound to the planar surface mainly as epoxy and tertiary alcohol groups, and to the sheet edges as carbonyl and carboxyl groups. An AFM image of graphene oxide is presented in figure 3. [18–21]

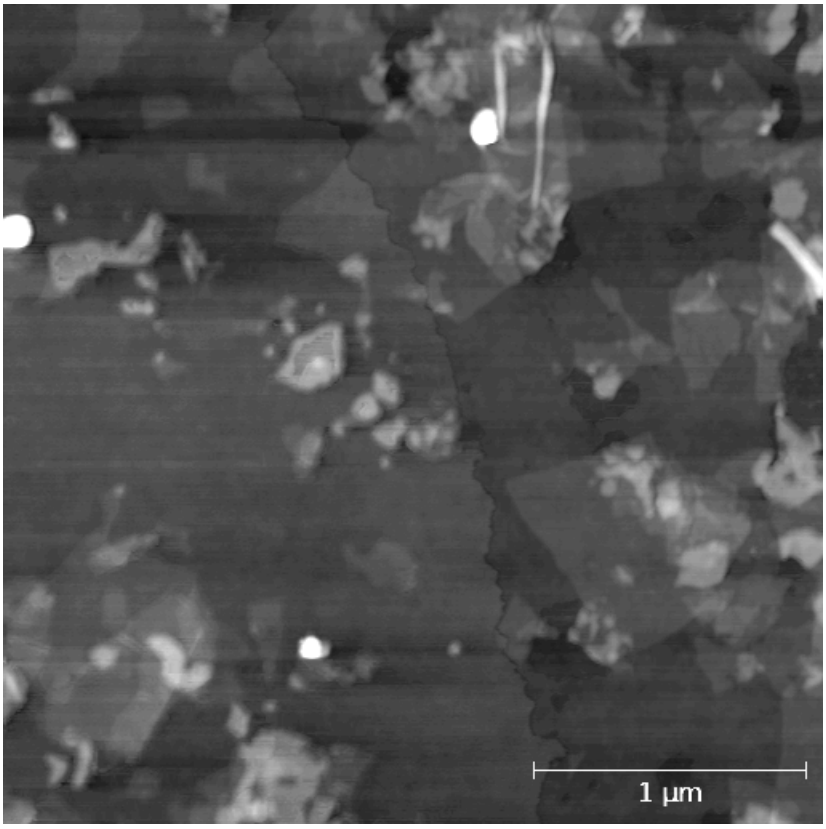


Figure 3. AFM image of graphene oxide showing sheets of GO.

3.1.2 Synthesis

The first report concerning the oxidation of graphene was by B.C. Brodie in 1859 who added potassium chlorate ($KClO_3$) to graphite in nitric acid (HNO_3)

while studying the atomic weight of graphite [22]. In 1898 the process was modified by L. Staudenmaier who added the $KClO_3$ in multiple doses and increased the acidity with sulfuric acid (H_2SO_4) [23]. The typical method used today is the method developed by Hummers and Offeman [24]. Graphite is added to a mixture of Potassium permanganate ($KMnO_4$) and sodium nitrate ($NaNO_3$) in concentrated sulfuric acid.

Marcano *et al.* produced GO that is more oxidized and has a more regular structure compared to the GO produced by Hummers method [25]. They excluded the $NaNO_3$, increased the amount of $KMnO_4$, and performed the reaction in a 9:1 mixture of sulphuric acid and phosphoric acid. In addition of being more oxidized and having more regular structure, this method does not produce toxic gases such as NO_2 and N_2O_4.

A fast and efficient method to produce GO has been reported by Shen *et al.* [26]. Graphite and benzoyl peroxide (BPO) are mixed at 110 °C in an open system for 10 min. The carbon dioxide created in this reaction increases the interlayer distance in graphite oxide, which makes it easier to exfoliate.

3.1.3 Properties

As the sp^2 structure of graphene is disrupted by the oxidation, GO is not electrically conductive. The conductivity can be quickly restored by reducing the oxygen functionalities. Xu *et al.* have demonstrated that the conductivity increases rapidly when the epoxides are reduced and more slowly when other oxygen functionalities are reduced [21]. For completely reduced graphene oxide they reached a conductivity of $1.5 \cdot 10^5$ S/m.

The defects of graphene oxide can also introduce some properties that are not present in pure graphene. For example the optical properties of GO can be tuned by functionalization or reduction. The photoluminescence of GO has been redshifted by hydrazine reduction and its fluorescence emission has been blueshifted by covalently grafting polyethylene glycol (PEG) to the surface of GO. [27–30] According to Eda *et al.* the photoluminescence of GO depends on the interactions between the sp^2 and sp^3 hybiridized sites meaning that the

photoluminescence emissions can be tuned by controlling the sp^2 sites [30].

3.1.4 Reduction of Graphene Oxide

The disrupted sp^2 structure of graphene oxide can be partially restored by reduction which can be done either chemically or thermally. [18]

Reduction by hydrazine monohydrate [31] is the most common chemical method used for GO reduction. Other chemicals used for the reduction of GO include sodium borohydride ($NaBH_4$), hydroquinone, and gaseous hydrogen. A problem with the chemical reductions is the introduction of heteroatomic impurities. For example the reduction by hydrazine results in nitrogen covalently bound to the reduced graphene oxide, which results in n-doped graphene. [18]

Graphite oxide can be exfoliated and reduced thermally. Heating of graphite oxide results in the formation of carbon dioxide from the oxygen functionalities of GO, which creates pressure between the GO sheets in graphite oxide and thus helps to exfoliate the sheets. [21,32]

3.2 Other means for producing graphene

Because the graphene sheets produced by oxidation and reduction are non-stoichiometric and defective, alternative methods for the large scale production of graphene are being studied. These methods are based on the expanded graphite used in batteries and fuel cells. The three common methods are producing graphene from graphite intercalation compounds (GIC), graphite's liquid phase exfoliation and electrochemical exfoliation of graphite. [27] As pure graphene is insoluble in most solvents and it has no functional groups that could be covalently functionalized, it's more challenging to functionalize than GO or RGO.

4 Functionalization of Graphene

Graphene as a material is unsoluble and unreactive, and it coalescents into graphite, so it often needs to be functionalized before it can be used in composites or for other applications. The most common functionalization is the oxidation to graphene oxide, which was discussed in the previous chapter. Further functionalization is usually done by covalently bonding an agent into the carboxyl or epoxy groups of graphene oxide. Graphene's functionalization can also be done by π-π interactions or Van der Waals forces.

In this chapter we first discuss the most common goals and applications of functionalizing graphene, followed by a look on the common covalent and non-covalent functionalizations.

4.1 Goals and Applications for Functionalizing Graphene

4.1.1 Solubility Improvement

The biggest obstacles in the use of graphene in composites are its insolubility in most solvents and its tendency to aggregate [14]. This means that the most common goal for functionalization is to improve graphene's solubility and dispersibility. The common way to achieve this is to oxidize graphite and exfoliate the formed graphite oxide to get a stable aqueous dispersion of graphene oxide (GO). GO is often a precursor for other functionalizations such as producing soluble reduced graphene oxides (RGO) [14,33–55], grafting ATRP initiators to the surface of graphene [45,55,56,56–59], or as a water soluble carrier for drugs [29,52,60]. Figure 4 shows the proposed reactions of functionalizing graphene oxide with isocyanate [49].

A composite can be produced by simply mixing the solutions and removing the solvent if graphene and the other components can be dissolved and dispersed in the same solvent [16]. Chemicals used to enhance graphenes solubility in water and other solvents are listed in table 1.

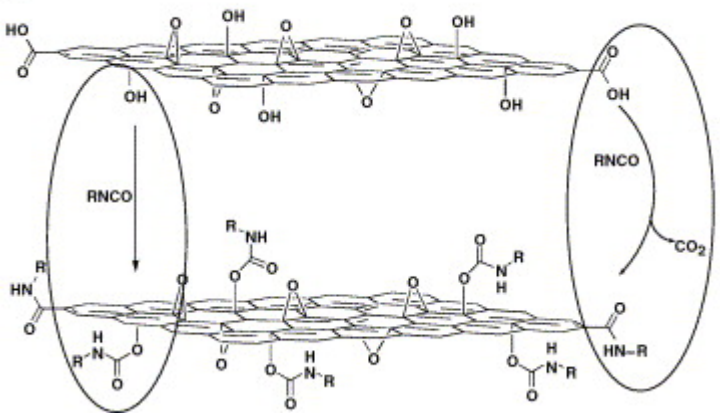


Figure 4. The proposed reactions of functionalizing graphene oxide with isocyanate. [49]

Table 1. Chemicals used to enhance the solubility of graphene in water and organic solvents

Chemical	Solvents
1-pyrenebutyrate [39]	Water
Azide group containing compounds [53]	Water, DMF, CCl_4, toluene
Chitosan [52]	Water
Ionic liquids (IL) [34,44]	Water, DMF, and DMSO
Isocyanate [33,49]	DMF, acetone, DMSO
Octadecylamine (ODA) [47,48,50]	DMAc, THF, 1,2-dichloroethane, Toluene, CCl_4, chlorobenzene
PDMAEMA [45]	Water (pH 1), methanol
PEO-b-PPO-b-PEO [41]	Water
Poly(norepinephrine) [54]	Water
Poly(sodium 4-styrenesulfonate) [43]	Water
Poly(tert-butyl acrylate) (PtBA) [55]	Organic solvents (THF, CCl_4, DMF)
Poly(vinyl alcohol) (PVA) [46]	DMSO, hot water
Salts containing aromatic molecules [35,38,51]	Water, DMF, DMAc, NMP
Sulfonated polyaniline (SPANI) [42]	Water
Sulfonic acid [37]	Water
TCNQ anion [40]	Water

4.1.2 Polymer Grafting

In addition to mixing dispersions of the wanted components of a composite, polymers can also be directly grown from the surface of graphene. For this purpose an initiator can be covalently attached to the surface of GO or RGO or the polymerization can be done by using the functional groups present in

GO. Examples of ATRP initiators grafted to graphene are presented in table 2. Examples of polymers grafted to graphene with or without previously grafted ATRP initiator are listed in table 3. [45,55–59,61–64]

Table 2. ATRP initiators grafted to the surface of graphene oxide

2-bromo-2-methylpropionyl bromide [45]
2-bromopropionyl bromide [56,59]
Alpha-bromoisobutyryl bromide [57]
Benzyl chloride [55]

Table 3. Graphene polymer composites created by polymer grafting.

3-aminopropyltriethoxysilane (APTS) [62]
Epoxy [58]
PDMAEMA [45]
Poly(allylamine) (PAAm) [61]
Poly(butyl acrylate) (PBA) [57]
Poly(methyl methacrylate) (PMMA) [57]
Poly(tert-butyl acrylate) (PtBA) [55]
Poly(vinyl alcohol) (PVA) [63]
Polyaniline (PANI) [64]
Polystyrene (PS) [56,57,59]

4.1.3 Doping

Graphene can be functionalized into a p-type semiconductor by doping it with electron withdrawing oxygen functionalities or by metals with higher electron affinity than graphene. Similarly it can be functionalized into a n-type semiconductor by doping it with electron donating nitrogen functionalities or alkaline metals. [27]

4.1.4 Bandgap creation

Graphene is a zero bandgap material which means that in its pure form it can't be used for transistors. To create a bandgap, graphene needs to be attached to a suitable substrate such as silicon. An other option is to use graphene nanoribbons but they are difficult to produce and for the bandgap to exists, the edge needs to have the arm-chair conformation which makes their large scale production even more difficult. [27]

4.2 Covalent Functionalization

4.2.1 Functionalization at the Carboxyl Group of Graphene Oxide

Prior to the covalent functionalization of the carboxyl group, the acid often needs to be activated. The activation is usually done by thionyl chloride ($SOCl_2$) [47,65–67], a carbodiimide [46,60] or by 2-(7-azabenzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU) [68]. After activation, addition of a nucleophile, such as an amine or a hydroxyl, results in a functional group covalently attached to GO through amidation or esterification. [18]

4.2.2 Functionalization at the Epoxy Group of Graphene Oxide

Ring-opening reactions can be used to modify the epoxy groups on the planar surface of graphene oxide. Octadecylamine [48], ionic liquids with an amine end group [44], and APTS [62] have been used for the ring-opening reactions. GO sheets have also been cross-linked by the epoxy groups through the addition of PAAm, which improved the mechanical properties of GO paper made from the cross-linked material [61]. Oh *et al.* have functionalized the epoxy group with alcohols which resulted in an ether and hydroxyl group being formed, and reduced the number of defects [69]. A schematic of the functionalization by alcohols is presented in figure 5.

4.2.3 Functionalization at the Hydroxyl Group of Graphene Oxide

Isocyanates can be used to form urethanes from the hydroxyl functionalities of GO's alcohols and carboxylic acids. Such functionalization results in the material no longer being soluble in water, but, instead, makes it soluble in polar aprotic solvents such as DMF, acetone, and DMSO. [33,49]

Liu *et al.* used oxalic acid, HOOC-COOH, to functionalize the hydroxyl groups of graphene oxide. Before functionalization, they used HBr to open the epoxide

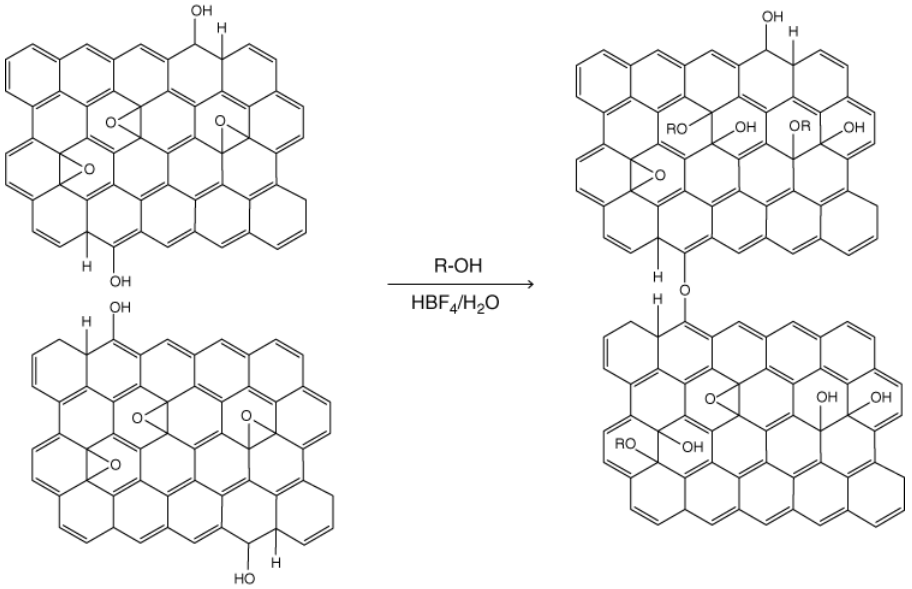


Figure 5. A schematic showing the functionalization of graphene oxide with alcohols. [69]

groups of graphene oxide. This way the only functional group present after functionalization were carboxyl groups on both the planar surface and the sheet edges. The repulsive interaction between the carboxyl groups enhanced the dispersablity of the as functionalized GO in aniline. [70]

4.3 Non-covalent Functionalization

The non-covalent functionalizations of graphene and GO are based on the π-π interactions of aromatic molecules, such as aniline, or Van der Waals forces. Non-covalent functionalizations do not disturb the sp^2 structure of graphene meaning that no defects are formed. Aromatic molecules that have been used for the non-covalent functionalization of graphene include pyrene derivatives such as pyrene butanoic acid succidymidyl ester (PBASE) [71], perylene derivatives such as 3,4,9,10-perylenetetracarboxylic diimide bisbenzenesulfonic acid (PDI) [51], DNA [72], TCNQ [40], and polymers such as PANI [73–77], SPANI [42,78], polypyrrole (PPy) [79–84], and PEO-*b*-PPO-*b*-PEO [41]. The functionalization with polymers can be done either by adsorbing the monomer to the surface of graphene [74–77,79,80,82–84], or by adsorbing a polymer chain to the surface of graphene [41,73,81].

5 Polyaniline-Graphene Composites

Polyaniline (PANI) is an easy to synthesize, environmentally stable conducting polymer that has high controllable conductivity and good electrochemical properties [85]. These properties make it an interesting material for a variety of applications including sensors, electrorheological materials, and electrodes e.g. for supercapacitors. [64,70,74,86–89]. It's produced by the oxidative polymerization of aniline either by using electrochemical polymerization or by using an oxidant such as ammonium persulfate $(NH_4)_2S_2O_8$. The general structure of polyaniline is shown in figure 6 and the conducting, HCl doped version in figure 7. [90]

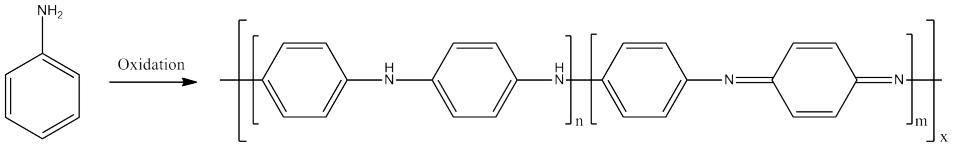


Figure 6. Polyaniline is produced by oxidizing aniline. X is half the degree of polymerization, n = 0, and m = 1 when the polymer is fully reduced (Leucoemeraldine), and n = 1, m = 0 when it's fully oxidized (Pernigraniline) [91].

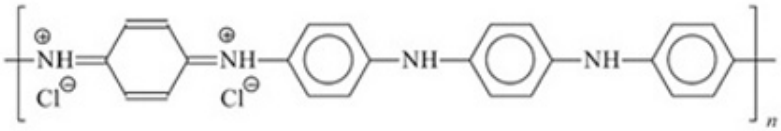


Figure 7. Structure of conducting HCl doped polyaniline. [92]

PANI and graphene both have aromatic benzene rings, which provides for strong π-π bonding between these materials. They both have also interesting electrical and other properties that provide interesting possibilities for composites. Usually the composite is fabricated by in sity polymerization where the aniline and graphene are dissolved in HCl solution and then the aniline is polymerized using a chemical oxidant [64,70,77,86,93]. In case non-conductive PANI is wanted, the acid may be omitted [87]. In cases where the aniline is polymerized electrochemically, aniline is usually first attached to graphene and then polymerized using sulfuric acid solution as the electrolyte [76,88,89].

Polyaniline has been studied for use as an electrode material for supercapacitors, but it lacks in charge storage capability and cyclic stability [89,94]. To remedy these shortcomings, PANI-graphene composites have been extensively

studied. Use of these composites as the electrode material in a supercapacitor have significantly improved the cyclic stability, and increased the storage capability of the electrode. [64,70,73,75,77,78,88,89]

Introduction of graphene to polyaniline has been found to increase the amount of active nucleation sites and provided excellent electron transfer pathways, which are interesting properties for use in sensor applications. PANI-graphene composites have been studied for at least dopamine and hydrogen detection with promising results. [74,86]

Polyaniline and graphene are also interesting materials for use in electrorheological (ER) fluid applications. An ER fluid consists of semiconducting or polarizable particles dispersed in a non-conducting liquid. The fluid turns from liquid to solid by the application of an electric field. A PANI-graphene oxide composite studied for such applications by Zhang *et al.* showed typical ER behaviour demonstrating its potential for application in ER smart materials. [87]

6 Polyurethane-Graphene Composites

Urethane is formed in a reaction between an isocyanate and a hydroxyl group. Thus a polyurethane requires at least a diol and a diisocyanate as monomers (figure 8). Having monomers with more than two of these functionalities results in increasingly branched polymers. Usually, polyurethanes involve a polyol, diol, and diisocyanate, where the polyol is a polyether or polyester, the diol is ethylene glycol, 1,4-butanediol, 1,6-hexanediol, or p-di(2-hydroxyethoxy)benzene, and the diisocyanate is hexamethylene diisocyanate (HDI), toluene diisocyanates (TDI), naphthalene 1,5-diisocyanate, or Methylene diphenyl diisocyanate (MDI). [90,95]

The variety of available monomers and controlling the reaction conditions provide for a wide range of different polyurethane products such as flexible and rigid foams and solid elastomers, extrusions, coatings, and adhesives. Polyurethanes are resistant to oil and grease and have good abrasion, tear,

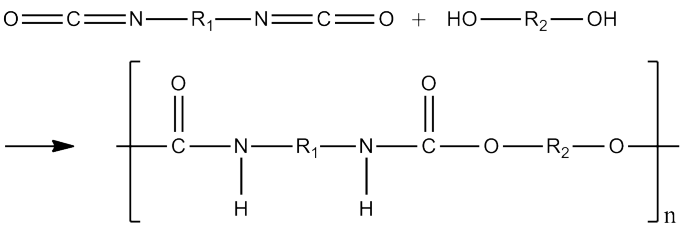


Figure 8. Generalized polyurethane reaction.

and impact resistance.They are used for example in furniture upholstery, roofing and insulation materials, forklift tires, and golf balls. [90]

Graphene oxide and reduced graphene oxide have hydroxyl-groups making them a sort of polyol and provide for the possibility of covalently bonding them to polyurethane using isocyanates. A straightforward way of fabricating a covalently bonded polyurethane-graphene oxide composite is to simply use graphene oxide as any other alcohol would be used in the polymerization reaction. As there are plenty of different methods to fabricate polyurethane and plenty of other reactions for utilizing the functional groups of graphene oxide, the method to fabricate PU-graphene composite varies greatly. It is also possible to create these composites by simple solution mixing as PU is soluble in DMF and GO can be dispersed in DMF or functionalized to be soluble in DMF [69,96–101]

As polyurethanes have a wealth of potential applications, the goals for fabricating PU-graphene composites are also plentiful. A common one is to simply use graphene to enhance the material's mechanical and electrical properties [97,99–101]. Other goals include, for example, the fabrication of shape memory materials [69], pressure sensitive foams [98], and infrared-triggered actuators [96].

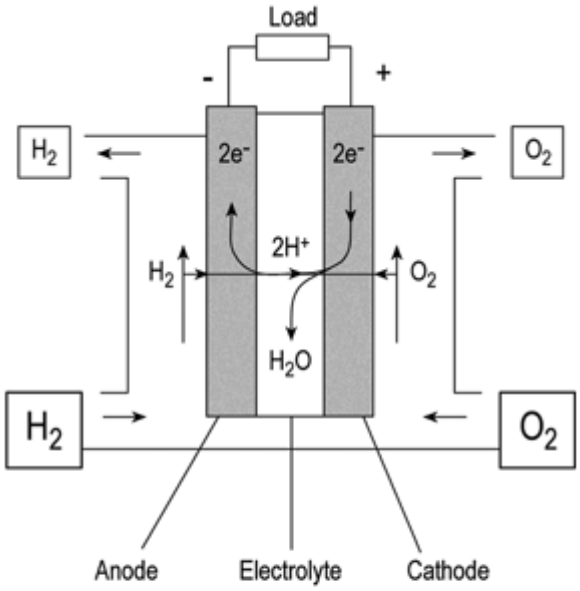
7 Applications for Graphene Composites

Graphene's properties make it an interesting material for a wide range of applications. This chapter takes a brief look in some potential applications for graphene composites.

7.1 Energy Applications

7.1.1 Fuel Cells

Fuel cells use an electrochemical reaction to convert the chemical energy of a fuel into electricity. The most common fuel used in a fuel cell is hydrogen. A fuel cell consists of two electrodes separated by a gastight electrolyte. The electrodes require high catalytic activity, high electrical conductivity, gas permeability, and chemical stability. Figure 9 illustrates the principle of a hydrogen fuel cell. [102]



Anode:	H_2	→	$2H^+ + 2e^-$
Cathode:	$1/2\ O_2 + 2H^+ + 2e^-$	→	H_2O
Overall reaction:	$H_2 + 1/2\ O_2$	→	H_2O

Figure 9. The operation of fuel cell with hydrogen as fuel and oxygen as oxidant. The electrodes are separated by a gastight electrolyte. [102]

Reduced graphene oxide has been studied as an electrocatalyst in a fuel cell. The power delivered by a RGO-Pt based fuel cell was 161 mW/cm^2 which is a 68 % improvement over an unsupported Pt based fuel cell. [103]

7.1.2 Solar Cells

Solar cells, or photovoltaic cells as they are also called, convert light into electric power. The main part of a solar cell is a semiconductor between two electrodes. [104]

For a dye-sensitized solar cell pyrenebutyrate modified graphene–poly(ethylene dioxythiophene) (PEDOT)–polystyrene sulfonic acid (PSS) composite has been used as the electrode material. The power conversion efficiency of the cell utilizing such composite was almost twice as high compared to a cell with only PEDOT:PSS as electrode material. [105] PEDOT:PSS-GO composite has also been used as a buffer layer for polymer solar cells by Yin *et al.* [106]. Indium tin oxide (ITO) electorde was coated with the composite to enhance the performance of the photovoltaic device. A Pt-GO composite fabricated by Yen *et al.* [107] increased the power conversion efficiency of a dye-sensitized solar cell by 20%.

An RGO-indium tin oxide (ITO) composite used as the photoanode in a dye-sensitized solar cell improved the energy conversion efficiency, light collection efficiency and charge transport rate of the cell [16]. RGO-pyrene-1-sulfonic acid sodium salt (PyS) composite film used as the anode in bulk heterojunction solar cell improved the overall power efficiency of the cell from 0.78 % to 1.12 % [51]. Poly(3-hexylthiophene) (P3HT) [108] and poly(3-alkyl thiophene) [109] have been used with isocyanate modified GO to produce composites to be used as the active layer in a bulk heterojunction photovoltaic device.

7.1.3 Supercapacitors

Supercapacitors are energy storage devices based on an electrochemical double-layer between high surface-area electrodes separated by a very thin electrolyte. Graphene has a high specific surface area so it is well suited for enhancing the performance of supercapacitor electrodes. [88,110,111]

Graphene's composites with conducting polymers such as polypyrrole (PPy) [79–81,83,84] and polyaniline [64,70,73,75–77,88,89] are often studied as elec-

trode materials for supercapacitors. The use of these composites improves the specific capacitance, rate capability and cycling stability of the capacitor.

7.2 Applications in Catalysis

Graphene's high specific surface area and electronic conductivity among other of its properties makes it a promising material for use in catalysts [112,113]. In addition to being studied for electrocatalysts used in fuel and solar cells [103,107], graphene composites have also been studied for catalysing oxidation reactions. An RGO-polymeric carbon nitride (g-C3N4) composite produced by Li *et al.* was used for catalysing selective oxidation of sp^3 C-H bonds [114]. This composite had good efficiency, high selectivity, and high stability.

7.3 Electrochemical Applications

Ye *et al.* [115] have functionalized graphene with polymeric protic ionic liquid (poly(1-vinyl-3-butylimidazolium) bromide) and used it in a composite with sulfonated polyimide. An electrolyte membrane fabricated from the composite showed an ionic conductivity of 0.75 S/m with 0.5 weight-% functionalized graphene, which was about 4 times higher than a similar electrode fabricated without functionalized graphene.

A graphene-SPANI composite electrode has been used for the fabrication of polyaniline (PANI) nanosheets. The fabricated PANI nanosheets had a capacitance five times higher than that of normal PANI. [78]

7.4 Electronics Applications

Graphene's high charge carrier mobility, thermal conductivity, mechanical strength, and specific surface area make it an interesting material for use in electronics such as field-effect transistors [116]. Eda *et al.* [117] have studied

a field-effect device fabricated using a composite of PS and isocyanate functionalized graphene. The performance of their device improved as the size of the used graphene sheets grew. An RGO-poly(vinyl alcohol) composite was used as a transparent electrode in flexible organic field-effect transistor by Lim *et al.*. Dispersing the composite in a solution of DMF and water, they were able to use inkjet printing for fabricating the electrodes. The field-effect devices with such electrodes exhibited high field-effect mobilites compared to commonly used alternatives. [116]

7.5 Medical and Biological Applications

As graphene oxide is water soluble and aromatic molecules can be adsorbed to its surface through Van der Waals and π-π interactions, it can be used as a carried for waterinsoluble aromatic drugs. A GO-PEG composite has been succesfully used as a carrier for cancer drugs such as doxorubicin [29] and the camptothecin analogue SN38 [60]. GO-Chitosan composite has been used as a carrier for camptothecin and gene delivery [52].

7.6 Sensors Applications

Graphene based nanocomposite films can potentially enhance the electrocatalytic acticity of electrochemical sensors and biosensors increasing the sensitivity of the device. Graphene has also a high surface-to-volume ratio which makes it effective for gas sensing. Graphene based sensors have been studied for at least hydrogen, carbon monoxide, dopamine, cancer cell, and H_2O_2 sensing. [74,76,86,118,119]

Al-Mashat *et al.* fabricated a hydrogen sensor based on RGO-PANI composite. The use of composite greatly enhanced the sensitivity of the sensor compared to a similar device fabricated using only graphene or PANI. [74]

Because the existing methods for dopamine detection are time-consuming, expensive, and have poor selectivity, an aptasensor based on graphene-PANI

composite was developed by Liu *et al.*. Their device was more selecive and had better limit of detection compared to conventional dopamine detection methods. It was also easy to fabricate and the method used is also suitable for creating other aptasensors. [86]

H_2O_2 is an important part in food, pharmaceutical, clinical, industrial, and environmental analyses, so its accurate determination is important. For the effective detection and electrocatalytic reduction of H_2O_2, sensors fabricated from graphene oxide-prussian blue composite film, and from HRP modified RGO-PANI composite have been studied. [76,118]

7.7 Applications in Optics

For the enhancement of the optical properties of graphene, amine functionalized phorphyrin and pyrrolidine fullerenes have been used. Such composites offer better nonlinear optical response compared to the individual components. [65,66]

Hou *et al.* [120] have functionalized graphene with oleic acid-modified magnetite nanoparticles to obtain magnetically active graphene. They used this material to produce a switch from of the polymeric microgel poly-(N-isopropylacrylamide) (PNIPAAm) for use in microreactors. The functionalized microgel could be controlled by near-infrared laser irradiation or by an external magnet. A sulfonated graphene-polyurethane composite that reacts to infrared light by contracting has been fabricated by Liang *et al.* [96]. An actuator fabricate from this material can lift a weight of 21.6 g 3.1 cm with 0.21 N of force.

EXPERIMENTAL PART

8 Research Goals

Graphene's excellent mechanical, thermal and electrical properties make it an interesting material for use in composites. Even in small amounts it has been shown to enhance these properties in its composites.

The objective of the experimental part was to study graphene polymer composites where graphene was functionalized by a chemical compound with two functional groups. For this purpose hexamethylene diisocyanate (HDI) was used to functionalize graphene oxide and the product was then used in polyurethane (PU) and polyaniline (PANI) composites. The composition, and the electrical and thermal properties of the fabricated composites were then studied.

9 Experimental

Graphene-polymer Nanocomposites were fabricated with polyurethane (PU) or polyaniline (PANI) as the matrix, and graphene oxide (GO) or HDI functionalized graphene oxide (f-GO) as the filler. In PU-GO and PU-f-GO composites, filler percentages were 0.5, 1.5, and 4.5 w-%. In PANI-f-GO composites filler percentages were 0.5 and 1,5 w-%.

9.1 Materials

Graphite flakes (particle size < 150 μm), $NaNO_3$, $KMnO_4$, H_2SO_4 (98.00 % purity), H_2O_2 (36 w-% purity), HCl (32 w-% purity), hexamethylene diisocyanate (HDI, 1,6-Diisocyanatohexane, 98.00 % purity), KBr, methylene bis(phenyl isocyanate) (MDI, 98.00 % purity), aniline (99.50 % purity), Hydrazine hydrate (reagent grade), and Ammonium persulfate (98.00 % purity) were acquired from Sigma-Aldrich. N,N-Dimethylformamide (DMF, 99.50 %

purity) and methylene chloride (Dichloromethane, 99.80 % purity) were purchased from Merck. Toluene (99.90 % purity) and N-Methyl-2-Pyrrolidone (NMP, 100 % purity) were procured from VWR. 1,3-Propanediol (98.00 % purity) was from Acros Organics and Polypropylene glycol P2000 (PPG) was from Fluka.

9.2 Production of Graphite Oxide

Graphite was oxidized by a modified Hummer's method. 2 g of graphite flakes, 1 g of $NaNO_3$, and 6 g of $KMnO_4$ were added to 50 ml of H_2SO_4. The mixture was then heated under 35 °C for 1 h. Then, first 150 ml of water was added to the mixture, and after 30 minutes another 200 ml of water and 5 ml of H_2O_2 were added. The mixture was then washed first with 10 w-% HCl and then with water until the pH of the mixture was 7. The product was dried overnight to obtain graphite oxide.

9.3 Functionalization of Graphite Oxide

1 g of graphite oxide was added to 50 ml DMF under nitrogen. Then 10 mmol HDI was added. The mixture was then stirred under nitrogen overnight. The next day, the mixture was poured into methylene chloride to coagulate the product. The product was filtered, washed with methylene chloride and dried.

The functionalized graphite oxide was analyzed by FT-IR (Mattson 3000 FTIR Spectrometer) from a KBr tablet to ascertain the presence of isocyante as well as to study its composition compared to graphene oxide. Isocyanate's absorbtion band shows in an IR spectra between 2000 and 2280 cm^{-1} [121].

9.4 Fabrication of Polymer Composites

9.4.1 Preparation of Polyurethane Composites

f-GO was added to 50 ml DMF in a 100 ml three-neck round bottom flask, and sonicated for 60 minutes. After sonication MDI was added. The reaction vessel was then heated to the reaction temperature, 80 °C under nitrogen, and PPG and 1,3-propanediol were injected with a syringe. The mixture was then left to polymerize overnight. The next day the mixture was centrifuged to remove any left over graphene, after which the polymer dissolved in DMF was precipitated by decanting the supernate to 250 ml water. The precipitated polymer was collected by centrifugation and dried overnight in vacuum. Figure 10 has a schematic illustrating the reaction.

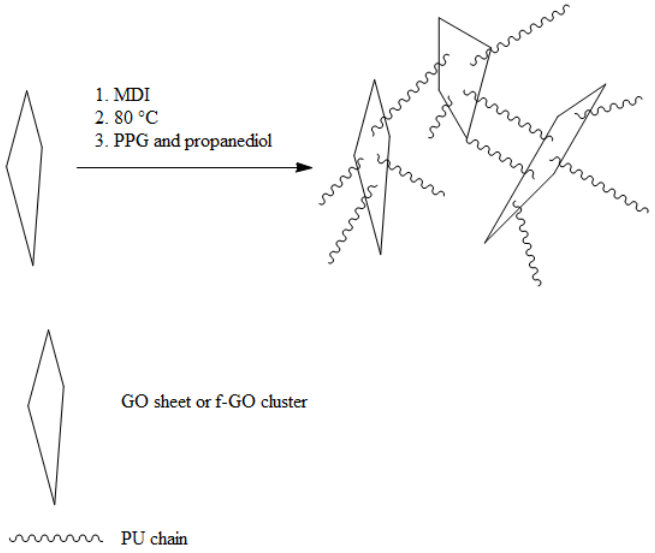


Figure 10. Fabrication of PU-GO and PU-f-GO composites. First MDI is added to the GO or f-GO dispersed in DMF. The reaction vessel is then heated to 80 °C under nitrogen, and then PPG and 1,3-propanediol are added.

As graphene oxide has hydroxide groups that are active in the reaction, the amounts of PPG and propanediol were adjusted to maintain some level of consistency in the hydroxyl-isocyanate ratio. Measured chemicals added to polymerizations of polyurethane and its composites are shown in table 4.

In order to study if the f-GO in a PU-f-GO composite can be reduced by

Table 4. Chemicals measured for the polymerizations of polyurethane and its composites.

Sample	MDI (g)	PPG (g)	1,3-propanediol (ml)	GO/f-GO (g)
PU	1.717	2.920	0.38	-
PU-GO-0.5	1.714	2.880	0.38	0.031
PU-GO-1.5	1.719	2.816	0.37	0.097
PU-GO-4.5	1.712	2.658	0.35	0.283
PU-f-GO-0.5	1.714	2.878	0.38	0.031
PU-f-GO-1.5	1.712	2.813	0.37	0.097
PU-f-GO-4.5	1.709	2.678	0.35	0.281

hydrazine hydrate, some of the PU-f-GO composite with 4.5 w-% f-GO was reduced. 1 gram of PU-f-GO-4.5 was dissolved in 50 ml DMF and heated to 95 °C. Then 0.5 ml of hydrazine was added and the mixture was left stirring for 2 h. Then the mixture was poured into water to coagulate the composite, which was then separated by centrifugation, and dried overnight in vacuum. The resulting material is hereafter referred to as r-PU-f-GO-4.5.

9.4.2 Preparation of Polyaniline Composites

Polyaniline-f-GO composites were fabricated with 0, 0.5, and 1.5 w-% f-go by oxidizing aniline with ammonium persulfate. These composites are referred to as PANI, PANI-f-GO-0.5 and PANI-f-GO-1.5 respectively. The functionalized graphene oxide was dissolved in 5 ml aniline in a 10 ml beaker. The solution was then sonicated for 1 h after which the mixture was centrifuged to remove all undissolved f-GO. Ammonium persulfate was added to 500 ml 0.5 M HCl in a 1000 ml erlenmeyer flask. Then the aniline-f-GO mixture was added dropwise to the erlenmeyer under vigorous stirring. The mixture was left to polymerize overnight. The composite was then filtered, washed with water, and dried in vacuum overnight. Figure 11 has a schematic of the reaction.

9.5 Characterization of Composites

FTIR analysis from a KBr tablet for the finished composites was carried out to study the composition of the fabricated materials.

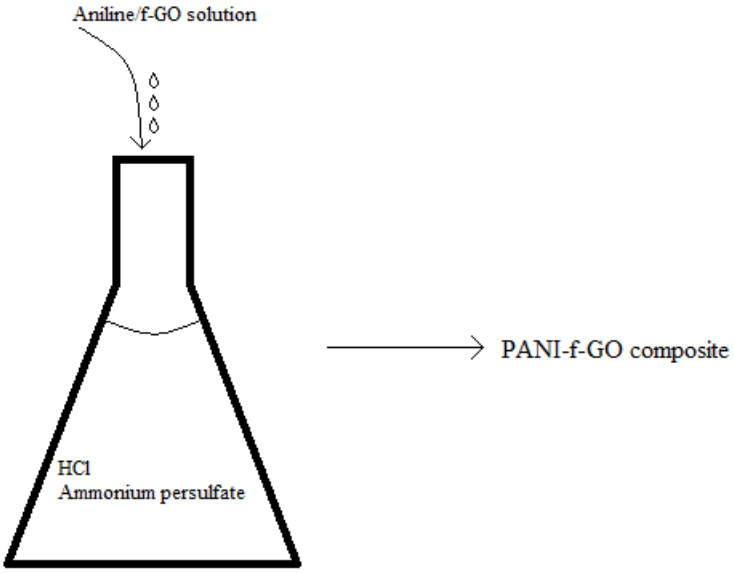


Figure 11. The method used to polymerize aniline/f-GO solution to PANI-f-GO composite. Aniline/f-GO solution is added dropwise to ammonium persulfate/HCl solution under vigorous stirring.

For analysing their electrical and mechanical conductivities, 1 mm thick and 10 mm diameter tablets were were pressed from the composites with 150 kN force using a Fontijne TP 400 hydraulic press. PANI and its composites were pressed in 50 °C for 5 minutes and PU and its composites were pressed in 190 °C also for 5 minutes.

Electrical conductivities were measured in room temperature with 4 point probe measurement (Jandel RM3000 Resistivity meter). Thermal conductivities were measured by transient plane source method (Hot disk thermal constants analyzer) in room temperature.

The 4-point probe measurement gives a sheet resistance in $\Omega/\square$. According to the device manual, to obtain a better result for the tablet used here, the measured resistance needs to be corrected by a thickness correction factor (0.9215) and a diameter correction factor (4.1712 / 4.532 = 0.92039). This can then be converted to bulk resistivity ($\Omega \cdot cm$) by multiplying with sample thickness in cm (0.1). [122]

Thermoanalytical analysis of the polyurethane composites was carried out by

differential scanning calorimetry (DSC, Mettler TOLEDO STAR^e DSC821^e). The device was run from 0 °C to 250 °C with scanning rate of 10 °C per minute. Polyurethane composites' molecular weights were measured with GPC (Waters 2000 Alliance) using toluene as the solvent. DSC was omitted for PANi composites, because it would only have shown the disintegration temperatures of the HCl used for doping, and then of the polymer. The gases released by the disintegrations might have been harmful for the equipment. As PANI is not soluble in common solvents, it could not be studied by GPC.

Atomic force microscopy analysis was carried out for PANI-f-GO-0.5, PU-GO-0.5 and PU-f-GO-1.5 to ascertain the presence of graphene sheets in the composites. The device (Dimension 5000, Veeco Inc) was used in tapping mode and the images were taken using a silicon tip (MicroMasch, 325 kHz, 46 N/m). The samples were prepared on a 1 cm x 1 cm glass sheet using DMF as the solvent for PU composites and NMP for the PANI composite.

10 Results and Discussion

10.1 Functionalized Graphene Oxide

The functionalization of graphene oxide with HDI resulted in a black powder resembling graphene oxide to the naked eye. Unlike GO, the functionalized version was unsoluble in water or other common solvents including DMF, NMP, chloroform, and toluene. GO functionalized by a monoisocyanate is soluble in DMF [33,49] but the diisocyanate functionalized GO produced here was not. However, the product was observed to be slightly soluble in aniline so, for the polyaniline composites, the f-GO was dissolved in aniline before polymerization.

The unsolubility of functionalized graphene oxide is probably due to the functionalization crosslinking the graphene oxide sheets, forming a mass of graphene oxide sheets that are randomly covalently bonded by HDI to each other. This could be considered a polyurethane where graphene oxide acts as the polyol.

Infrared spectroscopy was used to study the effects of functionalization. The IR spectra for GO and f-GO are presented in figure 12. These results show the presence of isocyanate in the latter, which means that not all isocyanate groups have reacted with the hydroxyl functionalities of graphite oxide.

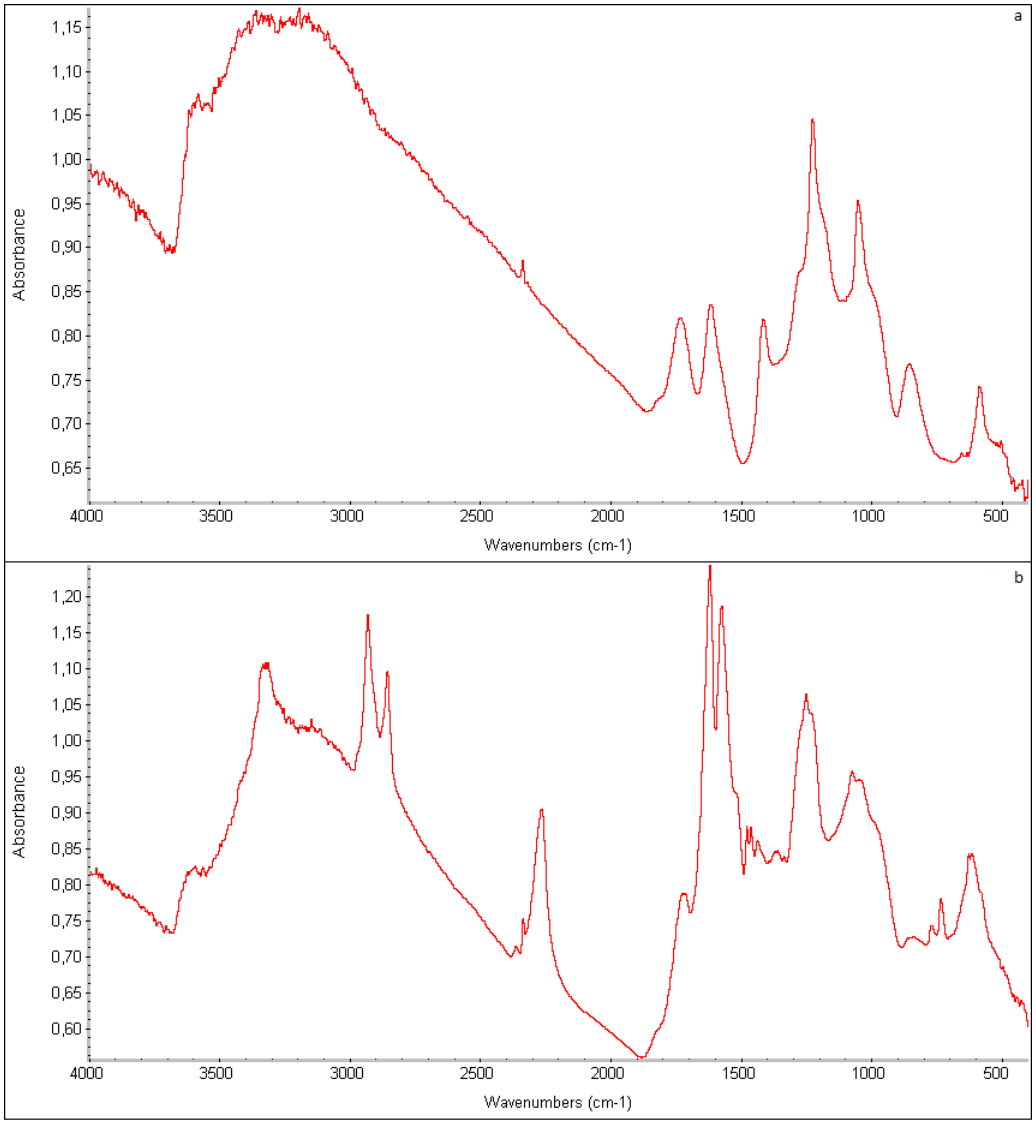


Figure 12. The FTIR spectra of (a) graphite oxide and (b) HDI functionalized graphite oxide.

In graphene oxides IR spectrum the most predominant feature is the strong and broad band in about 2500-3500 cm^{-1} caused by O-H stretching vibrations. This band covers other possible absorption bands in the same region. The presence of alcohols is further demonstrated by the strong band at about 1250 cm^{-1} which is likely caused by alcohols' C-O stretching vibrations. The band at about 1050 cm^{-1} is likely due to the asymmetrical stretching vibrations of C-O-C of graphene oxide's epoxides. The epoxides' asymmetrical ring stretching is

the likely cause for the band at around 850 cm^{-1}. The symmetrical stretching of epoxide rings might also cause a band at 1250 cm^{-1} but it is covered by the C-O band from the alcohols. The absorption band near 1750 cm^{-1} is likely caused by the carboxylic acid's C=O stretch and the band around 1400 cm^{-1} is probably due to the C-O-H bending of the acids. The bands at 1600 and 600 cm^{-1} are likely caused by the substituted benzene rings of graphene oxide. [121]

The most obvious change in the IR spectrum of HDI functionalized graphene oxide is the significantly lower intensity of the broad O-H stretching band and the appearance of the isocyanate band at 2280 cm^{-1}. Other obvious changes are the appearance of N-H stretching band around 3320 cm^{-1}, two C-H stretching bands at 2850 and 2950 cm^{-1} arising from the methylene chain of HDI, and the two intense bands at 1580 and 1620 cm^{-1}. The one at about 1620 cm^{-1} is probably the C=O stretching vibrations of the urethane and the one at about 1580 cm^{-1} is likely due to urethanes N-H bending vibrations. The alcohol's band at about 1250 cm^{-1} is replaced by a band caused by C-N-H vibrations. The band caused by epoxides around 850 cm^{-1} is all but vanished which indicates that the isocyanate has also reacted with the epoxides. The band at about 1100 cm^{-1} is likely caused by -C(=O)-O and C-N stretching vibrations of the urethane. The weak band around 720 cm^{-1} may be due to methylene rocking vibrations in the HDI. [121]

10.2 Polyaniline Composites

The fabricated polyaniline composites were extremely fine green dusts. After synthesis, an infrared spectroscopy was carried out for the composites to ascertain that f-GO was actually present in the composites but after multiple attemps no decent FTIR spectra could be obtained. Fortunately, the AFM image (figure 13) of the composite shows the presence of graphene sheets.

The results of the thermal and electrical conductance measurements of the composites and a commercial polyaniline product, PANIPOL CX by Panipol OY, can be found in table 5. For easier comparison, the electrical resistances are shown in figure 14 and thermal conductivities in figure 15.

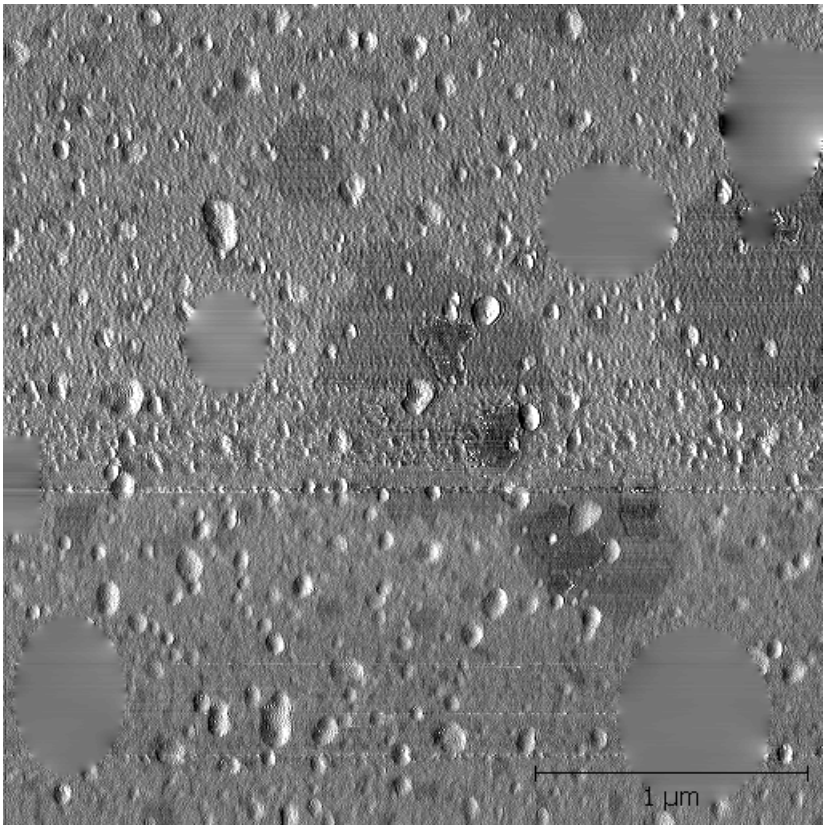


Figure 13. The AFM phase image of PANI-f-GO-0.5 showing the presence of graphene sheets. (The unclear areas are image mask used to remove impurities with extreme height.)

Table 5. Conductivity results for polyaniline, its composites, and a commercial polyaniline product. (TC = Thermal conductivity, TD = Thermal diffusivity, c = Specific heat capacity, SR = Sheet resistance, CSR = Corrected sheet resistance, BR = Bulk resistivity.)

Sample	TC ($\frac{W}{m \cdot K}$)	TD ($\frac{mm^2}{s}$)	c ($\frac{MJ}{m^3 \cdot K}$)	SR ($\frac{\Omega}{\square}$)	CSR	BR ($\Omega \cdot cm$)
PANI	0.072	0.201	0.323	352	299	29.9
PANI-f-GO 0.5	0.097	0.186	0.521	147	125	12.5
PANI-f-GO 1.5	0.072	0.220	0.346	171	145	14.5
PANIPOL CX	0.208	0.078	2.689	1000	848	84.8

These results show lower resistance for the composites over PANI but there doesn't seem to be a major difference between the two composites suggesting that the maximum amount of f-GO that is soluble in aniline is already present in the composite with less f-GO. Compared to the commercial polyaniline, the fabricated PANI and its composites have lower resistance but thermal conductivity is lower. Even though PANIPOL is less electrically conducting, it was easily processable, whereas the fabricated composites were fine powders

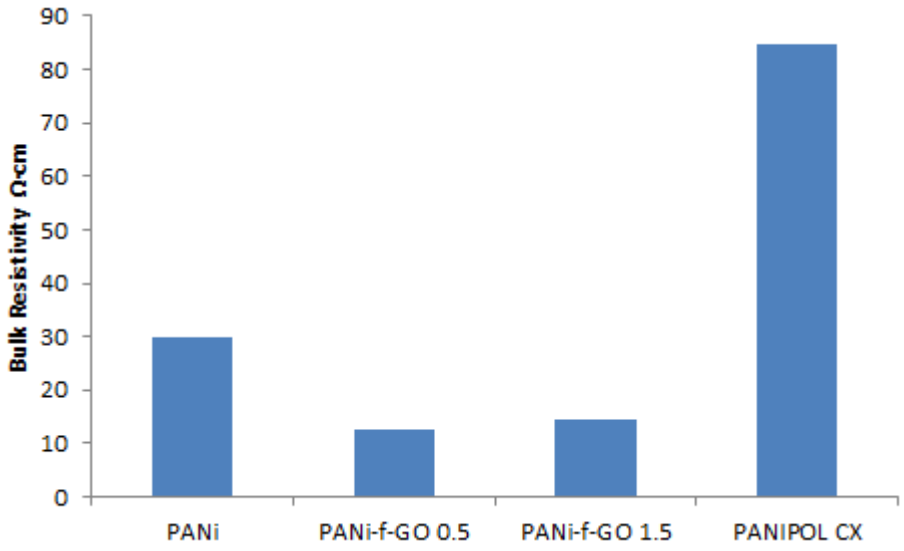


Figure 14. The electrical resistances of PANI, its composites, and a commercial polyaniline product.

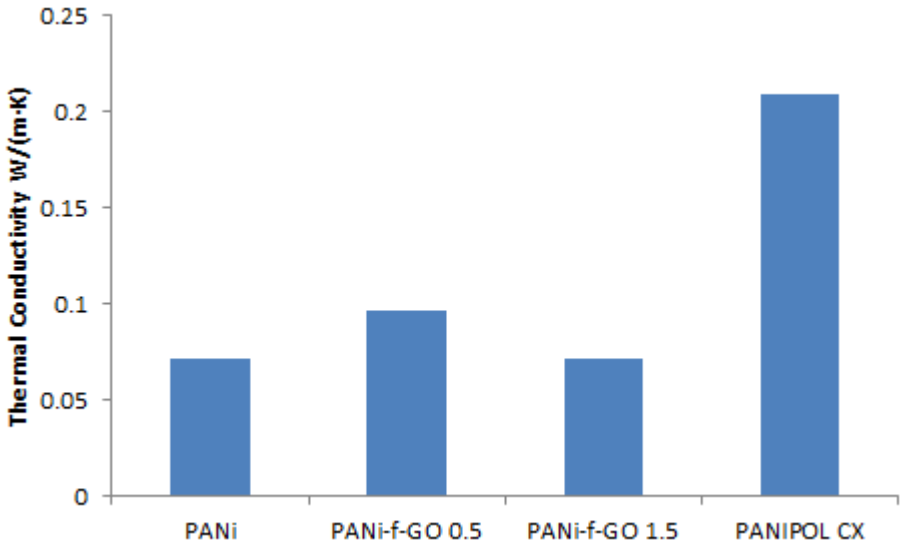


Figure 15. The thermal conductivities of PANI, its composites, and a commercial polyaniline product.

that are insoluble in common solvents, and the tablets pressed from them were quite fragile.

The International Union of Pure and Applied Chemistry (IUPAC) technical report about polyaniline found electrical conductivities to be between 2 and 17 $\frac{S}{cm}$ for HCl doped PANI. Converted to resistance these are between 0.06-0.5 $\Omega \cdot cm$, which are about 60 to 500 times less than for the pure polyaniline fab-

ricated here. This is probably due to differences in the preparation processes, e.g. temperature control of the reaction, and the method of introducing aniline to the reaction mixture. [123]

The thermal conductivities for the fabricated polyaniline is very low and the results from the two composites are inconclusive as to whether the filler affects the thermal conductivity. The results from polyurethane (discussed in 10.3) indicate that the addition of f-GO first slightly increases thermal conductivity but then rapidly decrease it. This could also be the case here, but that would contradict the electrical conductivity results by suggesting that more f-GO has dissolved in aniline which is unlikely. In literature, values of 0.07-0.28 $\frac{W}{m \cdot K}$ have been reported for HCl doped polyaniline in room temperature [124–127]. The values obtained here are similar to the values reported in literature.

10.3 Polyurethane Composites

The polyurethane and its composites fabricated in this work could be best described to be wax-like in composition. The pure polyurethane was grayish white, but as the percentage of GO and f-GO increased, the materials started to get a yellow hue.

After the composites were fabricated, an FTIR analysis was carried out for pure PU, PU-GO-1.5, and PU-f-GO-1.5. The spectra are presented in figure 16.

As seen from the IR spectra, the PU and PU-GO spectra are all but identical, but the PU-f-GO spectra shows a definite band for isocyanate at 2280 cm^{-1}. This band is probably carried over from f-GO, which also had a clear band for isocyanate, whereas in PU and PU-GO the isocyanate has reacted to form urethane.

The IR spectrum of the pure polyurethane shows cleary the N-H stretching vibrations at 3320 cm^{-1} and the C-H stretching bands at 2950 , 2910, 2890, and 2870 cm^{-1} which arise from the methyl- and methylene groups of PPG, propanediol and MDI. The aromatic C-H stretches from MDI are barely not-

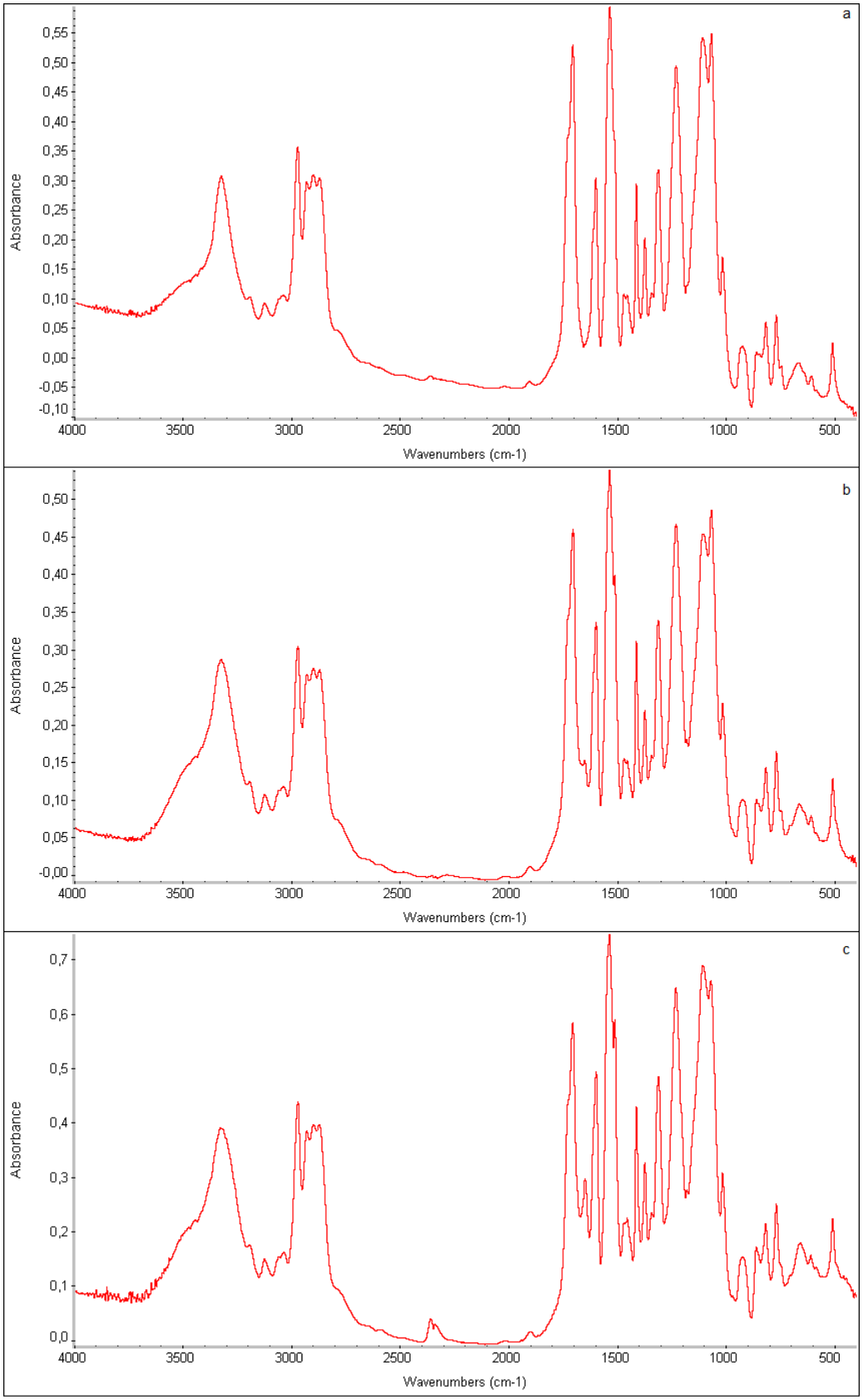


Figure 16. The FTIR spectra of (a) polyurethane, (b) polyurethane-GO composite with 1.5 w-% GO and (c) polyurethane-f-GO composite with 1.5 w-% f-GO.

icable at 3030 and 3120 cm^{-1}. The urethane's C=O group causes the bands around 1680 and 1320 cm^{-1}. The 1680 cm^{-1} is higher than the C=O band of f-GO due to the benzene rings of MDI. N-H bending vibrations are likely to be responsible for the band at 1550 cm^{-1}. C-H bending vibrations cause the weak and medium bands at 1470, 1400, and 1350 cm^{-1}. The bands at 1600 and below 1000 cm^{-1} are likely to be caused by the aromatic benzene rings. The aromatic C-N bond of MDI causes a strong band at 1220 cm^{-1}. PPG's ether and the C-CO-N of urethane cause two strong bands at about 1100 cm^{-1}. [121]

The spectra of PU-GO and PU-f-GO are very close to the spectrum of pure polyurethane. In addition to the isocyanate band in f-GO's spectrum at around 2350 cm^{-1}, the only changes seem to be the bands at about 1650 and 1500 cm^{-1}. The former is caused either by conjugated ketones, or alkenes in the graphene oxide sheets. The latter is likely due to benzene rings in graphene. The spectra has also a notable lack of bands associated with carboxylic acid, such as the broad O-H stretch at around 3000-3500 cm^{-1} or the ketone around 1700 cm^{-1}. This indicates that either the carboxylic acid has also reacted with MDI to form urethane and carbon dioxide, or the bands are simply covered by the bands already present in polyurethane's spectrum. [121]

To ascertain that graphene sheets are indeed present in the composites, AFM analysis was carried out to PU-GO-0.5 and PU-f-GO-1.5. The phase image of PU-GO-0.5 is shown in figure 17 (a) and the height image of PU-f-GO-1.5 is shown in figure 17 (b). The images show clearly that graphene sheets are present in the PU-GO composite and that f-GO blocks are present in the PU-f-GO composite.

The produced polyurethane and its composites felt wax like which indicated a low molecular weight. The GPC results in table 6 indeed indicate that the molecular weights are only about 5000. A result this low is probably due to the GPC solvent being toluene into which the fabricated polyurethanes were not readily soluble. As the molecular weights were so low, no study on the materials mechanical properties could be carried out.

None of the polyurethane composites were electrically conducting. Their thermal conductivities, diffusivities and heat capacities are listed in table 7. For

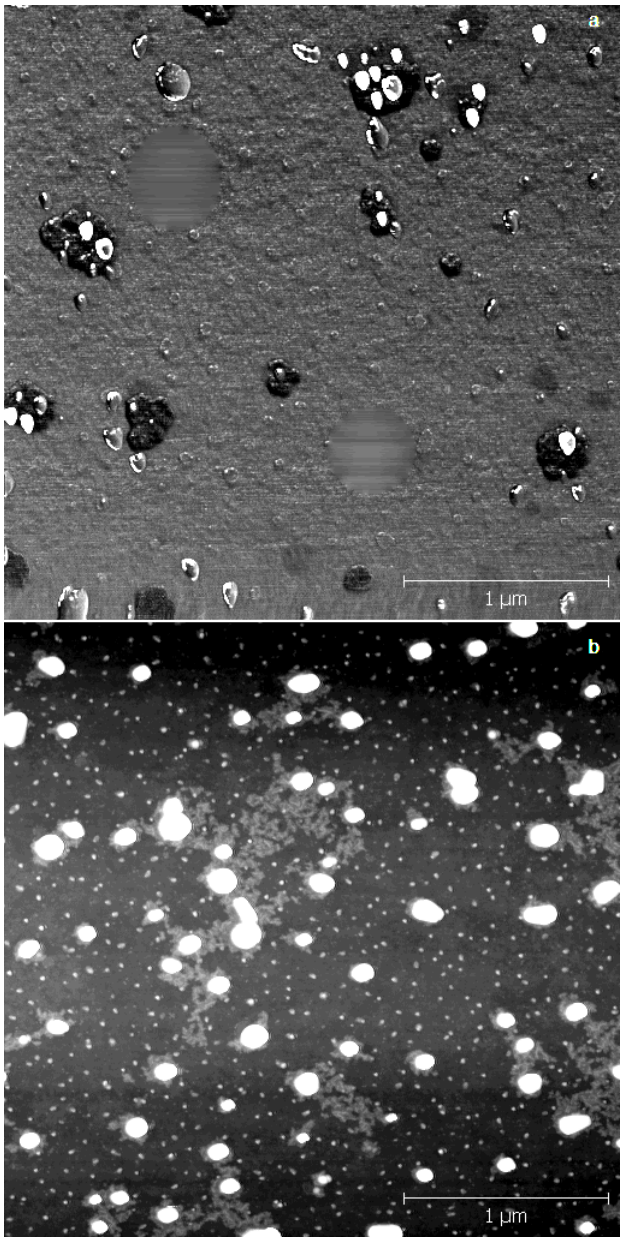


Figure 17. The AFM images of polyurethane composites: (a) The AFM phase image of PU-GO-0.5 and (b) the AFM height image of PU-f-GO-1.5.

Table 6. GPC results for PU and its composites.

Sample	Mw	Mn	MP	Polydispersity
PU	7400	6300	5900	1.17
PU f-GO 0.5	5700	5300	5400	1.08
PU GO 0.5	6400	5800	5600	1.10
PU f-GO 1.5	5300	4900	5100	1.08
PU f-GO 4.5	5300	4700	5100	1.11
PU GO 4.5	5200	4900	5100	1.08
PU GO 1.5	5600	5100	5300	1.10
r-PU-f-GO 4.5	5700	5100	5500	1.12

easier comparison of the thermal conductivities, they are also presented as a column diagram in figure 18.

Table 7. Thermal conductivity results for polyurethane and its composites. TC = Thermal conductivity, TD = Thermal diffusivity, and c = Specific heat capacity

Sample	TC ($\frac{W}{m \cdot K}$)	TD ($\frac{mm^2}{s}$)	c ($\frac{MJ}{m^3 \cdot K}$)
PU	0.219	0.150	1.46
PU-GO-0.5	0.216	0.123	1.76
PU-GO-1.5	0.207	0.114	1.81
PU-GO-4.5	0.199	0.125	1.59
PU-f-GO-0.5	0.223	0.151	1.48
PU-f-GO-1.5	0.193	0.101	1.91
PU-f-GO-4.5	0.170	0.084	2.02
r-PU-f-GO-4.5	0.200	0.155	1.38

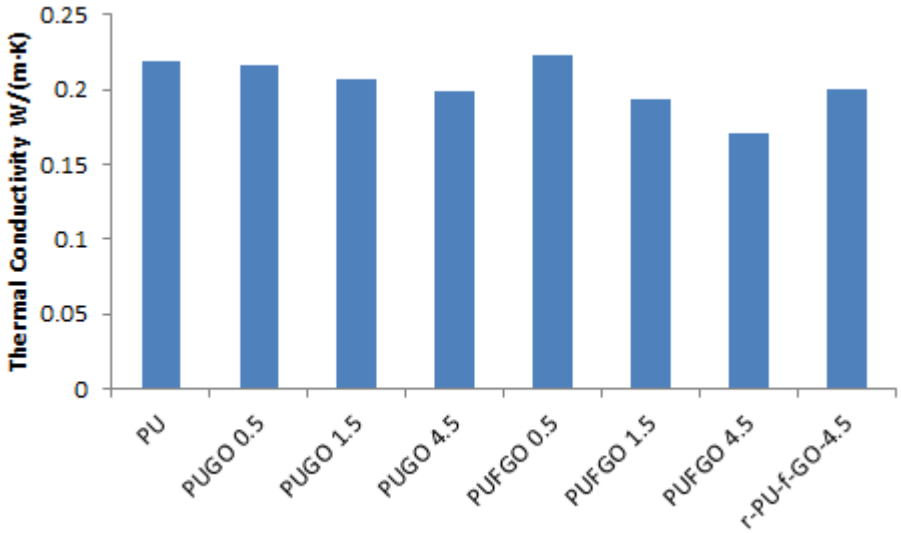


Figure 18. The thermal conductivities of PU and its composites.

The thermal data shows that the conductivities get lower with the addition of GO or f-GO. The addition of f-GO lowers the conductivity more rapidly than GO. This indicates that the crystalline structures in pure polyurethane are disturbed by the addition of a filler, and the filler does not improve heat transfer. The reduction of PU-f-GO-4.5 increased the thermal conductivity slightly suggesting an increase in the crystallinity of the material. These observations are further evident in the DSC results discussed below.

To further study the thermal properties of the polyurethane composites DSC analysis was carried out. The results are shown in figure 19 for unreduced composites, and in figure 20 the curves of PU-f-GO-4.5 and r-PU-f-GO-4.5 are compared. The data is from the heating curve giving the melting points of polyurethane.

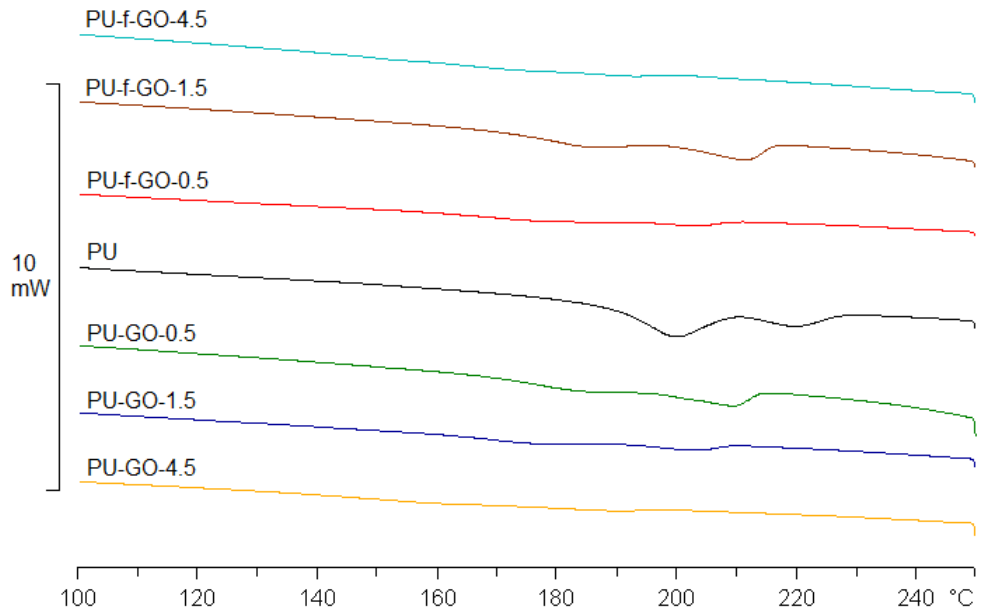


Figure 19. The DSC results of PU and its composites.

From the DSC data we can see that there are two melting points for both the hard and soft segments of polyurethane. For the pure polyurethane these points are at 200 °C and 220 °C. These melting points get lower and less clear with increasing. For the composites with 4.5 w-% filler the melting points are almost nonexistent. The straightening of the DSC curves indicate that the crystalline parts of pure polyurethane are no longer present in the composites. The reduction of PU-f-GO-4.5 has increased the melting points by about 5 °C, which suggests an increase in the crystallinity. This is likely due to

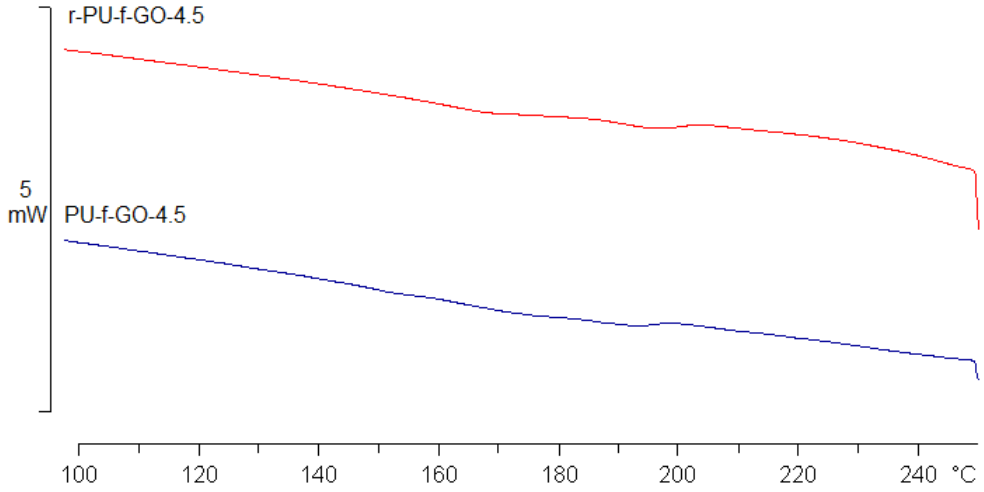


Figure 20. The DSC results of r-PU-f-GO-4.5 compared to the results of PU-f-GO-4.5.

the polyurethane chains being more and more loosely packed with increasing amount of GO or f-GO, thus requiring less energy to melt the polymer chains.

The reduction seems to restore some of the crystallinity of the polyurethane strands. This is likely caused by the removal of the oxygen functionalities that cause repulsive interactions in the material. This allows for closer packing of the polyurethane chains. Nevertheless the reduced composite was not electrically or thermally conducting.

The DSC curves of PU-f-GO-1.5 and PU-GO-0.5, and PU-f-GO-0.5 and PU-GO-1.5 are very much alike, which suggests mislabeling of two of the samples. As the curves of the composites with the most filler show almost no change the possibly mislabeled ones are likely to be PU-f-GO-0.5 and PU-f-GO-1.5.

11 Conclusions

Unsolubility of the functionalized graphene oxide suggests that HDI has cross-linked the graphene oxide sheets resulting in an insoluble powder. This material is not a very useful filler to enhance the thermal, electrical, or mechanical properties of polymer composites. The material may be useful for applica-

tions that require porous materials such as gas adsorption or supercapacitor electrodes, but this was not studied in the scope of this work.

Even though polyurethanes are known to have a wide variety of applications, the wax-like polyurethane here is clearly not useful in applications that require any kind of mechanical strength. It could potentially have uses in coatings and adhesives.

Using f-GO and GO in polyurethane composites resulted in nearly identical results indicating that the separate functionalization of GO had extremely little use for the PU composites fabricated in this work. None of the PU-composites were electrically conducting and their thermal conductivity decreased. Thus highly conductive PU composites can not be produce by the method specified in this work.

The polyaniline composites' electrical conductance improved slightly compared to pure polyaniline, but the very small differences between the composites indicate that maximum amount of f-GO has dissolved in aniline already in the composite with less f-GO. As the polyaniline composites are insoluble powders and the tablets that were pressed from them were fragile, they are not very useful materials used as such, but they might be used as fillers in other composites or as particles in electrorheological fluids.

12 Suggestions for Future Research

The diisocyanate functionalization of graphene oxide produces a potentially extremely porous material. If the functionalized material could be fabricated in a way that resulted in a material that is more easily processable and utilizable, this material could then potentially be used for many applications such as gas adsorption and high surface area electrodes.

The wax-like polyurethane composites did not have mechanical strength, but they were readily solvable in DMF, meaning they have potential applications used in adhesives and coatings. Graphene-based polyurethane composites are

not yet extensively studied for such applications, so studying a PU-GO composite as a coating material, e.g. for paper, would be an interesting research topic.

An other interesting research topic would be to study composites made with PANI, PU, and GO. For example the effect of PANI-GO composite as a filler in polyurethane and PU-GO composite used as filler in polyaniline. This way, for example the conductivity properties of PANI and graphene could potentially be introduced to the processability of polyurethane.

References

1. Geim, A. K., Novoselov, K. S., The rise of graphene, *Nature Materials* **6** (2007) 183–191.

2. Bolotin, K. I., Sikes, K. J., Jiang, Z., Klima, M., Fudenberg, G., Hone, J., Kim, P., Stormer, H. L., Ultrahigh electron mobility in suspended graphene, *Solid State Communications* **146** (2008) 351–355.

3. Morozov, S. V., Novoselov, K. S., Katsnelson, M. I., Schedin, F., Elias, D. C., Jaszczak, J. A., Geim, A. K., Giant intrinsic carrier mobilities in graphene and its bilayer, *Physical Review Letters* **100** (2008) 016602.

4. Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., Firsov, A. A., Electric field effect in atomically thin carbon films, *Science* **306** (2004) 666–669.

5. Lee, C., Wei, X., Kysar, J. W., Hone, J., Measurement of the elastic properties and intrinsic strength of monolayer graphene, *Science* **321** (2008) 385–388.

6. Seol, J. H., Jo, I., Moore, A. L., Lindsay, L., Aitken, Z. H., Pettes, M. T., Li, X., Yao, Z., Huang, R., Broido, D., Mingo, N., Ruoff, R. S., Shi, L., Two-dimensional phonon transport in supported graphene, *Science* **328** (2010) 213–216.

7. Cai, W., Moore, A. L., Zhu, Y., Li, X., Chen, S., Shi, L., Ruoff, R. S., Thermal transport in suspended and supported monolayer graphene grown by chemical vapor deposition, *Nano Letters* **10** (2010) 1645–1651.

8. Balandin, A. A., Ghosh, S., Bao, W., Calizo, I., Teweldebrhan, D., Miao, F., Lau, C. N., Superior thermal conductivity of single-layer graphene, *Nano Letters* **8** (2008) 902–907.

9. Nair, R. R., Blake, P., Grigorenko, A. N., Novoselov, K. S., Booth, T. J., Stauber, T., Peres, N. M. R., Geim, A. K., Fine structure constant defines visual transparency of graphene, *Science* **320** (2008) 1308–1308.

10. Xia, F., Mueller, T., ming Lin, Y., Valdes-Garcia, A., Avouris, P., Ultrafast graphene photodetector, *Nature Nanotechnology* **4** (2009) 839–843.

11. Yoo, B. M., Shin, H. J., Yoon, H. W., Park, H. B., Graphene and graphene oxide and their uses in barrier polymers, *Journal of Applied Polymer Science* **131** (2014) 39628.

12. Aizawa, T., Souda, R., Otani, S., Ishizawa, Y., Oshima, C., Anomalous bond of monolayer graphite on transition-metal carbide surfaces, *Physical Review Letters* **64** (1990) 768–771.

13. Berger, C., Song, Z., Li, X., Wu, X., Brown, N., Naud, C., Mayou, D., Li, T., Hass, J., Marchenkov, A. N., Conrad, E. H., First, P. N., de Heer, W. A., Electronic confinement and coherence in patterned epitaxial graphene, *Science* **312** (2006) 1191–1196.

14. Li, D., Müller, M. B., Gilje, S., Kaner, R. B., Wallace, G. G., Processable aqueous dispersions of graphene nanosheets, *Nature Nanotechnology* **3** (2008) 101–105.

15. Gómez-Navarro, C., Meyer, J. C., Sundaram, R. S., Chuvilin, A., Kurasch, S., Burghard, M., Kern, K., Kaiser, U., Atomic structure of reduced graphene oxide, *Nano Letters* **10** (2010) 1144–1148.

16. Bai, H., Li, C., Shi, G., Functional composite materials based on chemically converted graphene, *Advanced Materials* **23** (2011) 1089–1115.

17. Matte, H. S. S. R., Subrahmanyam, K. S., Rao, C. N. R., Novel magnetic properties of graphene: Presence of both ferromagnetic and antiferromagnetic features and other aspects, *The Journal of Physical Chemistry C* **113** (2009) 9982–9985.

18. Dreyer, D. R., Park, S., Bielawski, C. W., Ruoff, R., The chemistry of graphene oxide, *Chemical Society Reviews* **39** (2010) 228–240.

19. He, H., Riedl, T., Lerf, A., Klinowski, J., Solid-state nmr studies of the structure of graphite oxide, *The Journal of physical chemistry* **100** (1996) 19954–19958.

20. Lerf, A., He, H., Forster, M., Klinowski, J., Structure of graphite oxide revisited, *The Journal of Physical Chemistry B* **102** (1998) 4477–4482.

21. Xu, Z., Bando, Y., Liu, L., Wang, W., Bai, X., Golberg, D., Electrical conductivity, chemistry, and bonding alternations under graphene oxide to graphene transition as revealed by in situ tem, *ACS Nano* **5** (2011) 4401–4406.

22. Brodie, B. C., On the atomic weight of graphite, *Philosophical Transactions of the Royal Society of London* **149** (1859) 249–259.

23. Staudenmaier, L., Verfahren zur darstellung der graphitsäure, *Berichte der Deutschen Chemischen Gesellschaft* **31** (1898) 1481–1487.

24. Hummers, W. S., Offeman, R. E., Preparation of graphitic oxide, *Journal of the American Chemical Society* **80** (1958) 1339–1339.

25. Marcano, D. C., Kosynkin, D. V., Berlin, J. M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L. B., Lu, W., Tour, J. M., Improved synthesis of graphene oxide, *ACS Nano* **4** (2010) 4806–4814.

26. Shen, J., Hu, Y., Shi, M., Lu, X., Qin, C., Li, C., Ye, M., Fast and facile preparation of graphene oxide and reduced graphene oxide nanoplatelets, *Chemistry of Materials* **21** (2009) 3514–3520.

27. Loh, K. P., Bao, Q., Ang, P. K., Yang, J., The chemistry of graphene, *Journal of Materials Chemistry* **20** (2010) 2277–2289.

28. Luo, Z., Vora, P. M., Mele, E. J., Johnson, A. T., Kikkawa, J. M., Photoluminescence and band gap modulation in graphene oxide, *Applied Physics Letters* **94** (2009) 111909–3.

29. Sun, X., Liu, Z., Welsher, K., Robinson, J., Goodwin, A., Zaric, S., Dai, H., Nano-graphene oxide for cellular imaging and drug delivery, *Nano Research* **1** (2008) 203–212.

30. Eda, G., Lin, Y.-Y., Mattevi, C., Yamaguchi, H., Chen, H.-A., Chen, I.-S., Chen, C.-W., Chhowalla, M., Blue photoluminescence from chemically derived graphene oxide, *Advanced Materials* **22** (2010) 505–509.

31. Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S. T., Ruoff, R. S., Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon* **45** (2007) 1558–1565.

32. McAllister, M. J., Li, J.-L., Adamson, D. H., Schniepp, H. C., Abdala, A. A., Liu, J., Herrera-Alonso, M., Milius, D. L., Car, R., Prud'homme, R. K., Aksay, I. A., Single sheet functionalized graphene by oxidation and thermal expansion of graphite, *Chemistry of Materials* **19** (2007) 4396–4404.

33. Stankovich, S., Dikin, D. A., Dommett, G. H. B., Kohlhaas, K. M., Zimney, E. J., Stach, E. A., Piner, R. D., Nguyen, S. T., Ruoff, R. S., Graphene-based composite materials, *Nature* **442** (2006) 282–286.

34. Zhou, X., Wu, T., Ding, K., Hu, B., Hou, M., Han, B., Dispersion of graphene sheets in ionic liquid [bmim][pf6] stabilized by an ionic liquid polymer, *Chemical Communications* **46** (2010) 386–388.

35. Ghosh, A., Rao, K., George, S., Rao, C., Noncovalent functionalization, exfoliation, and solubilization of graphene in water by employing a fluorescent coronene carboxylate, *Chemistry - A European Journal* **16** (2010) 2700–2704.

36. Pham, V. H., Cuong, T. V., Hur, S. H., Oh, E., Kim, E. J., Shin, E. W., Chung, J. S., Chemical functionalization of graphene sheets by solvothermal reduction of a graphene oxide suspension in n-methyl-2-pyrrolidone, *Journal of Materials Chemistry* **21** (2011) 3371–3377.

37. Si, Y., Samulski, E. T., Synthesis of water soluble graphene, *Nano Letters* **8** (2008) 1679–1682.

38. Lomeda, J. R., Doyle, C. D., Kosynkin, D. V., Hwang, W.-F., Tour, J. M., Diazonium functionalization of surfactant-wrapped chemically converted graphene sheets, *Journal of the American Chemical Society* **130** (2008) 16201–16206.

39. Xu, Y., Bai, H., Lu, G., Li, C., Shi, G., Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets, *Journal of the American Chemical Society* **130** (2008) 5856–5857.

40. Hao, R., Qian, W., Zhang, L., Hou, Y., Aqueous dispersions of tcnq-anion-stabilized graphene sheets, *Chemical Communications* (2008) 6576–6578.

41. Zu, S.-Z., Han, B.-H., Aqueous dispersion of graphene sheets stabilized by pluronic copolymers: Formation of supramolecular hydrogel, *The Journal of Physical Chemistry C* **113** (2009) 13651–13657.

42. Bai, H., Xu, Y., Zhao, L., Li, C., Shi, G., Non-covalent functionalization of graphene sheets by sulfonated polyaniline, *Chemical Communications* (2009) 1667–1669.

43. Stankovich, S., Piner, R. D., Chen, X., Wu, N., Nguyen, S. T., Ruoff, R. S., Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate), *Journal of Materials Chemistry* **16** (2006) 155–158.

44. Yang, H., Shan, C., Li, F., Han, D., Zhang, Q., Niu, L., Covalent functionalization of polydisperse chemically-converted graphene sheets with amine-terminated ionic liquid, *Chemical Communications* (2009) 3880–3882.

45. Yang, Y., Wang, J., Zhang, J., Liu, J., Yang, X., Zhao, H., Exfoliated graphite oxide decorated by pdmaema chains and polymer particles, *Langmuir* **25** (2009) 11808–11814.

46. Veca, L. M., Lu, F., Meziani, M. J., Cao, L., Zhang, P., Qi, G., Qu, L., Shrestha, M., Sun, Y.-P., Polymer functionalization and solubilization of carbon nanosheets, *Chemical Communications* (2009) 2565–2567.

47. Niyogi, S., Bekyarova, E., Itkis, M. E., McWilliams, J. L., Hamon, M. A., Haddon, R. C., Solution properties of graphite and graphene, *Journal of the American Chemical Society* **128** (2006) 7720–7721.

48. Wang, S., Chia, P.-J., Chua, L.-L., Zhao, L.-H., Png, R.-Q., Sivaramakrishnan, S., Zhou, M., Goh, R. G. S., Friend, R. H., Wee, A. T. S., Ho, P. K. H., Band-like transport in surface-functionalized highly solution-processable graphene nanosheets, *Advanced Materials* **20** (2008) 3440–3446.

49. Stankovich, S., Piner, R. D., Nguyen, S. T., Ruoff, R. S., Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets, *Carbon* **44** (2006) 3342–3347.

50. Wang, J.-Y., Yang, S.-Y., Huang, Y.-L., Tien, H.-W., Chin, W.-K., Ma, C.-C. M., Preparation and properties of graphene oxide/polyimide composite films with low dielectric constant and ultrahigh strength via in situ polymerization, *Journal of Materials Chemistry* **21** (2011) 13569–13575.

51. Su, Q., Pang, S., Alijani, V., Li, C., Feng, X., Müllen, K., Composites of graphene with large aromatic molecules, *Advanced Materials* **21** (2009) 3191–3195.

52. Bao, H., Pan, Y., Ping, Y., Sahoo, N. G., Wu, T., Li, L., Li, J., Gan, L. H., Chitosan-functionalized graphene oxide as a nanocarrier for drug and gene delivery, *Small* **7** (2011) 1569–1578.

53. He, H., Gao, C., General approach to individually dispersed, highly soluble, and conductive graphene nanosheets functionalized by nitrene chemistry, *Chemistry of Materials* **22** (2010) 5054–5064.

54. Kang, S. M., Park, S., Kim, D., Park, S. Y., Ruoff, R. S., Lee, H., Simultaneous reduction and surface functionalization of graphene oxide by mussel-inspired chemistry, *Advanced Functional Materials* **21** (2011) 108–112.

55. Li, G. L., Liu, G., Li, M., Wan, D., Neoh, K. G., Kang, E. T., Organo- and water-dispersible graphene oxide-polymer nanosheets for organic electronic memory and gold nanocomposites, *The Journal of Physical Chemistry C* **114** (2010) 12742–12748.

56. Fang, M., Wang, K., Lu, H., Yang, Y., Nutt, S., Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites, *Journal of Materials Chemistry* **19** (2009) 7098–7105.

57. Lee, S. H., Dreyer, D. R., An, J., Velamakanni, A., Piner, R. D., Park, S., Zhu, Y., Kim, S. O., Bielawski, C. W., Ruoff, R. S., Polymer brushes via controlled, surface-initiated atom transfer radical polymerization (atrp) from graphene oxide, *Macromolecular Rapid Communications* **31** (2010) 281–288.

58. Bao, C., Guo, Y., Song, L., Kan, Y., Qian, X., Hu, Y., In situ preparation of functionalized graphene oxide/epoxy nanocomposites with effective reinforcements, *Journal of Materials Chemistry* **21** (2011) 13290–13298.

59. Fang, M., Wang, K., Lu, H., Yang, Y., Nutt, S., Single-layer graphene nanosheets with controlled grafting of polymer chains, *Journal of Materials Chemistry* **20** (2010) 1982–1992.

60. Liu, Z., Robinson, J. T., Sun, X., Dai, H., Pegylated nanographene oxide for delivery of water-insoluble cancer drugs, *Journal of the American Chemical Society* **130** (2008) 10876–10877.

61. Park, S., Dikin, D. A., Nguyen, S. T., Ruoff, R. S., Graphene oxide sheets chemically cross-linked by polyallylamine, *The Journal of Physical Chemistry C* **113** (2009) 15801–15804.

62. Yang, H., Li, F., Shan, C., Han, D., Zhang, Q., Niu, L., Ivaska, A., Covalent functionalization of chemically converted graphene sheets via silane and its reinforcement, *Journal of Materials Chemistry* **19** (2009) 4632–4638.

63. Salavagione, H. J., Gomez, M. A., Martinez, G., Polymeric modification of graphene through esterification of graphite oxide and poly(vinyl alcohol), *Macromolecules* **42** (2009) 6331–6334.

64. Gao, Z., Wang, F., Chang, J., Wu, D., Wang, X., Wang, X., Xu, F., Gao, S., Jiang, K., Chemically grafted graphene-polyaniline composite for application in supercapacitor, *Electrochimica Acta* **133** (2014) 325–334.

65. Xu, Y., Liu, Z., Zhang, X., Wang, Y., Tian, J., Huang, Y., Ma, Y., Zhang, X., Chen, Y., A graphene hybrid material covalently functionalized with porphyrin: Synthesis and optical limiting property, *Advanced Materials* **21** (2009) 1275–1279.

66. Liu, Z.-B., Xu, Y.-F., Zhang, X.-Y., Zhang, X.-L., Chen, Y.-S., Tian, J.-G., Porphyrin and fullerene covalently functionalized graphene hybrid materials with large nonlinear optical properties, *The Journal of Physical Chemistry B* **113** (2009) 9681–9686.

67. Zhang, X., Huang, Y., Wang, Y., Ma, Y., Liu, Z., Chen, Y., Synthesis and characterization of a graphene–c60 hybrid material, *Carbon* **47** (2009) 334–337.

68. Mohanty, N., Berry, V., Graphene-based single-bacterium resolution biodevice and dna transistor: Interfacing graphene derivatives with nanoscale and microscale biocomponents, *Nano Letters* **8** (2008) 4469–4476.

69. Oh, S. M., Oh, K. M., Dao, T. D., il Lee, H., Jeong, H. M., Kim, B. K., The modification of graphene with alcohols and its use in shape memory polyurethane composites, *Polymer International* **62** (2013) 54–63.

70. Liu, Y., Deng, R., Wang, Z., Liu, H., Carboxyl-functionalized graphene oxide–polyaniline composite as a promising supercapacitor material, *Journal of Materials Chemistry* **22** (2012) 13619.

71. Wang, Y., Chen, X., Zhong, Y., Zhu, F., Loh, K. P., Large area, continuous, few-layered graphene as anodes in organic photovoltaic devices, *Applied Physics Letters* **95** (2009) 063302–3.

72. Lu, C.-H., Yang, H.-H., Zhu, C.-L., Chen, X., Chen, G.-N., A graphene platform for sensing biomolecules, *Angewandte Chemie International Edition* **48** (2009) 4785–4787.

73. Wu, Q., Xu, Y., Yao, Z., Liu, A., Shi, G., Supercapacitors based on flexible graphene/polyaniline nanofiber composite films, *ACS Nano* **4** (2010) 1963–1970.

74. Al-Mashat, L., Shin, K., Kalantar-zadeh, K., Plessis, J. D., Han, S. H., Kojima, R. W., Kaner, R. B., Li, D., Gou, X., Ippolito, S. J., Wlodarski, W., Graphene/polyaniline nanocomposite for hydrogen sensing, *The Journal of Physical Chemistry C* **114** (2010) 16168–16173.

75. Wang, H., Hao, Q., Yang, X., Lu, L., Wang, X., Effect of graphene oxide on the properties of its composite with polyaniline, *ACS Applied Materials & Interfaces* **2** (2010) 821–828.

76. Feng, X.-M., Li, R.-M., Ma, Y.-W., Chen, R.-F., Shi, N.-E., Fan, Q.-L., Huang, W., One-step electrochemical synthesis of graphene/polyaniline composite film and its applications, *Advanced Functional Materials* **21** (2011) 2989–2996.

77. Zhang, K., Zhang, L. L., Zhao, X. S., Wu, J., Graphene/polyaniline nanofiber composites as supercapacitor electrodes, *Chemistry of Materials* **22** (2010) 1392–1401.

78. Zhao, Y., Bai, H., Hu, Y., Li, Y., Qu, L., Zhang, S., Shi, G., Electrochemical deposition of polyaniline nanosheets mediated by sulfonated polyaniline functionalized graphenes, *Journal of Materials Chemistry* **21** (2011) 13978–13983.

79. Zhang, D., Zhang, X., Chen, Y., Yu, P., Wang, C., Ma, Y., Enhanced capacitance and rate capability of graphene/polypyrrole composite as elec-

trode material for supercapacitors, *Journal of Power Sources* **196** (2011) 5990–5996.

80. Liu, A., Li, C., Bai, H., Shi, G., Electrochemical deposition of polypyrrole/sulfonated graphene composite films, *The Journal of Physical Chemistry C* **114** (2010) 22783–22789.

81. Biswas, S., Drzal, L. T., Multilayered nanoarchitecture of graphene nanosheets and polypyrrole nanowires for high performance supercapacitor electrodes, *Chemistry of Materials* **22** (2010) 5667–5671.

82. Bose, S., Kuila, T., Uddin, M. E., Kim, N. H., Lau, A. K. T., Lee, J. H., In-situ synthesis and characterization of electrically conductive polypyrrole/graphene nanocomposites, *Polymer* **51** (2010) 5921–5928.

83. Bose, S., Kim, N. H., Kuila, T., tak Lau, K., Lee, J. H., Electrochemical performance of a graphene–polypyrrole nanocomposite as a supercapacitor electrode, *Nanotechnology* **22** (2011) 295202.

84. Xu, C., Sun, J., Gao, L., Synthesis of novel hierarchical graphene/polypyrrole nanosheet composites and their superior electrochemical performance, *Journal of Materials Chemistry* **21** (2011) 11253–11258.

85. Kim, K.-S., Park, S.-J., Influence of multi-walled carbon nanotubes on the electrochemical performance of graphene nanocomposites for supercapacitor electrodes, *Electrochimica Acta* **56** (2011) 1629 – 1635.

86. Liu, S., Xing, X., Yu, J., Lian, W., Li, J., Cui, M., Huang, J., A novel label-free electrochemical aptasensor based on graphene–polyaniline composite film for dopamine determination, *Biosensors and Bioelectronics* **36** (2012) 186–191.

87. Zhang, W. L., Liu, Y. D., Choi, H. J., Fabrication of semiconducting graphene oxide/polyaniline composite particles and their electrorheological response under an applied electric field, *Carbon* **50** (2012) 290–296.

88. Jiang, X., Setodoi, S., Fukumoto, S., Imae, I., Komaguchi, K., Yano, J., Mizota, H., Harima, Y., An easy one-step electrosynthesis of graphene/polyaniline composites and electrochemical capacitor, *Carbon* **67** (2014) 662–672.

89. Gao, Z., Yanga, W., Wang, J., Yan, H., Yao, Y., Ma, J., Wang, B., Zhang, M., Liu, L., Electrochemical synthesis of layer-by-layer reduced graphene oxide sheets/polyaniline nanofibers composite and its electrochemical performance, *Electrochimica Acta* **91** (2013) 185–194.

90. Odian, G., *Principles of Polymerization*, 4 edition, John Wiley & Sons, Inc, Hoboken, New Jersey, USA 2004, 29-32, 130-132, 165 p.

91. Feast, W. J., Tsibouklis, J., Pouwer, K. L., Groenendaal, L., Meijer, E. W., Synthesis, processing and material properties of conjugated polymers, *Polymer* **1996** (1996) 5017–5047.

92. Stejskal, J., Sapurina, I., Polyaniline: Thin films and colloidal dispersions (iupac technical report), *Pure and Applied Chemistry* **77** (2005) 815–826.

93. Gómez, H., Ram, M. K., Alvi, F., Villalba, P., Stefanakos, E. L., Kumar, A., Graphene-conducting polymer nanocomposite as novel electrode for supercapacitors, *Journal of Power Sources* **196** (2011) 4102–4108.

94. Naarmann, H., Polymers, electrically conducting, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA 2000.

95. Six, C., Richter, F., Isocyanates, organic, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA 2003.

96. Liang, J., Xu, Y., Huang, Y., Zhang, L., Wang, Y., Ma, Y., Li, F., Guo, T., Chen, Y., Infrared-triggered actuators from graphene-based nanocomposites, *The Journal of Physical Chemistry C* **113** (2009) 9921–9927.

97. Ding, J. N., Fan, Y., Zhao, C. X., Liu, Y. B., Yu, C. T., Yuan, N. Y., Electrical conductivity of waterborne polyurethane/graphene composites prepared by solution mixing, *Journal of Composite Materials* **46** (2012) 747–752.

98. R. M. Hodlur, M. K. R., Self assembled graphene layers on polyurethane foam as a highly pressure sensitive conducting composite, *Composites Science and Technology* **90** (2014) 160–165.

99. Wu, C., Huang, X., Wang, G., Wu, X., Yang, K., Li, S., Jiang, P., Hyperbranched-polymer functionalization of graphene sheets for enhanced mechanical and dielectric properties of polyurethane composites, *Journal of Materials Chemistry* **22** (2012) 7010–7019.

100. Kaveh, P., Mortezaei, M., Barikani, M., Khanbabaei, G., Low-temperature flexible polyurethane/graphene oxide nanocomposites: Effect of polyols and graphene oxide on physicomechanical properties and gas permeability, *Polymer-Plastics Technology and Engineering* **53** (2014) 278–289.

101. Chen, D., Chen, G., In situ synthesis of thermoplastic polyurethane/graphene nanoplatelets conductive composite by ball milling, *Journal of Reinforced Plastics* **32** (2013) 300–307.

102. Heinzel, A., Cappadonia, M., Stimming, U., Kordesch, K. V., de Oliveira, J. C. T., Fuel cells, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA 2010.

103. Kamat, P. V., Graphene-based nanoarchitectures. anchoring semiconductor and metal nanoparticles on a two-dimensional carbon support, *The Journal of Physical Chemistry Letters* **1** (2010) 520–527.

104. Pfisterer, F., Photovoltaic cells, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA 2000.

105. Hong, W., Xu, Y., Lu, G., Li, C., Shi, G., Transparent graphene/pedot–pss composite films as counter electrodes of dye-sensitized solar cells, *Electrochemistry Communications* **10** (2008) 1555–1558.

106. Yin, B., Liu, Q., Yang, L., Wu, X., Liu, Z., Hua, Y., Yin, S., Chen, Y., Buffer layer of pedot:pss/graphene composite for polymer solar cells, *Journal of Nanoscience and Nanotechnology* **10** (2010) 1934–1938.

107. Yen, M.-Y., Teng, C.-C., Hsiao, M.-C., Liu, P.-I., Chuang, W.-P., Ma, C.-C. M., Hsieh, C.-K., Tsai, M.-C., Tsai, C.-H., Platinum nanoparticles/graphene composite catalyst as a novel composite counter electrode for high performance dye-sensitized solar cells, *Journal of Materials Chemistry* .

108. Liu, Q., Liu, Z., Zhang, X., Yang, L., Zhang, N., Pan, G., Yin, S., Chen, Y., Wei, J., Polymer photovoltaic cells based on solution-processable graphene and p3ht, *Advanced Functional Materials* **19** (2009) 894–904.

109. Liu, Z., Liu, Q., Huang, Y., Ma, Y., Yin, S., Zhang, X., Sun, W., Chen, Y., Organic photovoltaic devices based on a novel acceptor material: Graphene, *Advanced Materials* **20** (2008) 3924–3930.

110. Halper, M. S., Ellenbogen, J. C., Supercapacitors: A brief overview, *Technical report*, MITRE Nanosystems Group (2006), URL `http://www.mitre.org/sites/default/files/pdf/06_0667.pdf`.

111. Somiya, S., *Handbook of Advanced Ceramics - Materials, Applications, Processing, and Properties (2nd Edition)*, Elsevier 2013, 164-166 p., URL `http://app.knovel.com/hotlink/toc/id:kpHACMAPP6/handbook-advanced-ceramics/handbook-advanced-ceramics`.

112. Machado, B. F., Serp, P., Graphene-based materials for catalysis, *Catalysis Science & Technology* **2** (2012) 54–75.

113. Zhou, X., Qiao, J., Yang, L., Zhang, J., A review of graphene-based nanostructural materials for both catalyst supports and metal-free catalysts in pem fuel cell oxygen reduction reactions, *Advanced Energy Materials* **4** (2014) 1301523.

114. Li, X.-H., Chen, J.-S., Wang, X., Sun, J., Antonietti, M., Metal-free activation of dioxygen by graphene/g-c3n4 nanocomposites: Functional dyads for selective oxidation of saturated hydrocarbons, *Journal of the American Chemical Society* **133** (2011) 8074–8077.

115. Ye, Y.-S., Tseng, C.-Y., Shen, W.-C., Wang, J.-S., Chen, K.-J., Cheng, M.-Y., Rick, J., Huang, Y.-J., Chang, F.-C., Hwang, B.-J., A new graphene-modified protic ionic liquid-based composite membrane for solid polymer electrolytes, *Journal of Materials Chemistry* **21** (2011) 10448–10453.

116. Lim, S., Kang, B., Kwak, D., Lee, W. H., Lim, J. A., Cho, K., Inkjet-printed reduced graphene oxide/poly(vinyl alcohol) composite electrodes for flexible transparent organic field-effect transistors, *The Journal of Physical Chemistry C* **116** (2012) 7520–7525.

117. Eda, G., Chhowalla, M., Graphene-based composite thin films for electronics, *Nano Letters* **9** (2009) 814–818.

118. Zhang, Y., Sun, X., Zhu, L., Shen, H., Jia, N., Electrochemical sensing based on graphene oxide/prussian blue hybrid film modified electrode, *Electrochimica Acta* **56** (2011) 1239 – 1245.

119. Feng, L., Chen, Y., Ren, J., Qu, X., A graphene functionalized electrochemical aptasensor for selective label-free detection of cancer cells, *Biomaterials* **32** (2011) 2930–2937.

120. Hou, C., Zhang, Q., Wang, H., Li, Y., Functionalization of pnipaam microgels using magnetic graphene and their application in microreactors as switch materials, *Journal of Materials Chemistry* **21** (2011) 10512–10517.

121. Silverstein, R. M., Webster, F. X., Kiemle, D. J., *Spectrometric Identification of Organic Compounds*, 7 edition, John Wiley & Sons, Inc, Hoboken, New Jersey, USA 2005, 72-126 p.

122. Jandel Engineering LTD, *RM3000 Test Unit Instructions*.

123. Stejskal, J., Gilbert, R. G., Polyaniline. preparation of a conducting polymer (iupac technical report), *Pure and Applied Chemistry* **74** (2002) 857–867.

124. Li, J., Tang, X., Li, H., Yan, Y., Zhang, Q., Synthesis and thermoelectric properties of hydrochloric acid-doped polyaniline, *Synthetic Metals* **160** (2010) 1153–1158.

125. Yan, H., Sada, N., Toshima, N., Thermal transporting properties of electrically conductive polyaniline films as organic thermoelectric materials, *Journal of Thermal Analysis and Calorimetry* **69** (2002) 881–887.

126. de Albuquerque, J. E., Melo, W. L. B., Faria, R. M., Determination of physical parameters of conducting polymers by photothermal spectroscopies, *Review of Scientific Instruments* **74** (2003) 306–308.

127. Jin, J., Wang, Q., Haque, M. A., Doping dependence of electrical and thermal conductivity of nanoscale polyaniline thin films, *Journal of Physics D: Applied Physics* **43** (2010) 205302.